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AIR POLLUTION ASPECTS OF ALDEHYDES

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Litton Systems, Incorporated
Bethesda, Maryland

September 1969

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AIR POLLUTION ASPECTS
OF
ALDEHYDES

Prepared for the
National Air Pollution Control Administration
Consumer Protection & Environmental Health Service
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FOREWORD

As the concern for air quality grows, so does the concern over the less ubiquitous but potentially harmful contaminants that are in our atmosphere. Thirty such pollutants have been identified, and available information has been summarized in a series of reports describing their sources, distribution, effects, and control technology for their abatement.

A total of 27 reports have been prepared covering the 30 pollutants. These reports were developed under contract for the National Air Pollution Control Administration (NAPCA) by Litton Systems, Inc. The complete listing is as follows:

Aeroallergens (pollens)
Aldehydes (includes acrolein and formaldehyde)
Ammonia
Arsenic and Its Compounds
Asbestos
Barium and Its Compounds
Beryllium and Its Compounds
Biological Aerosols (microorganisms)
Boron and Its Compounds
Cadmium and Its Compounds
Chlorine Gas
Chromium and Its Compounds (includes chromic acid)
Ethylene
Hydrochloric Acid
Hydrogen Sulfide
Iron and Its Compounds
Manganese and Its Compounds
Mercury and Its Compounds
Nickel and Its Compounds
Odorous Compounds
Organic Carcinogens
Pesticides
Phosphorus and Its Compounds
Radioactive Substances
Selenium and Its Compounds
Vanadium and Its Compounds
Zinc and Its Compounds

These reports represent current state-of-the-art literature reviews supplemented by discussions with selected knowledgeable individuals both within and outside the Federal Government. They do not however presume to be a synthesis of available information but rather a summary without an attempt to interpret or reconcile conflicting data. The reports are necessarily limited in their discussion of health effects for some pollutants to descriptions of occupational health exposures and animal laboratory studies since only a few epidemiologic studies were available.

Initially these reports were generally intended as internal documents within NAPCA to provide a basis for sound decision-making on program guidance for future research activities and to allow ranking of future activities relating to the development of criteria and control technology documents. However, it is apparent that these reports may also be of significant value to many others in air pollution control, such as State or local air pollution control officials, as a library of information on which to base informed decisions on pollutants to be controlled in their geographic areas. Additionally, these reports may stimulate scientific investigators to pursue research in needed areas. They also provide for the interested citizen readily available information about a given pollutant. Therefore, they are being given wide distribution with the assumption that they will be used with full knowledge of their value and limitations.

This series of reports was compiled and prepared by the Litton personnel listed below:

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ABSTRACT

The principal effect of low concentrations of aldehydes on humans and animals is primary irritation of the mucous membranes of the eyes, upper respiratory tract, and skin. Animal studies indicate that high concentrations can injure the lungs and other organs of the body. Aldehydes, particularly formaldehyde, may contribute to eye irritation and unpleasant odors that are common annoyances in polluted atmospheres. Aldehydes, either directly or indirectly, may also cause injury to plants.

Aldehyde emissions result from incomplete combustion of hydrocarbons and other organic materials. The major emission source appears to be vehicle exhaust, but significant amounts may be produced from incineration of wastes and burning of fuels (natural gas, fuel oil, and coal). In addition, significant amounts of atmospheric aldehydes can result from photochemical reactions between reactive hydrocarbons and nitrogen oxides. Moreover, aldehydes can react photochemically to produce other products, including ozone, peroxides, and peroxyacetyl nitrate compounds. Local sources of aldehydes may include manufacturing of chemicals and other industrial processes that result in the pyrolysis of organic compounds in air or oxygen.

Reported emission data from various sources have been compiled for aldehydes in general and for formaldehyde and acrolein. Initial ambient air measurements of aliphatic aldehydes by the National Air Sampling Network in 1967 indicate that the average concentrations for several cities range from 3 to 79 $\mu g/m^3$.

Control of aldehyde emissions is being studied along with current hydrocarbon (organic) control programs. However, the use of certain combustion control techniques, such as catalytic afterburners, may cause an increase in the amount of aldehydes emitted.

No information has been found on the economic costs of aldehyde air pollution or on the costs of its abatement.

Numerous analytical methods for determining "aldehydes," formaldehyde, and acrolein have been reported. Satisfactory colorimetric methods are available.

Two aldehydes--formaldehyde and acrolein--are of particular interest in the study of air pollution and have been given special attention in this report.

CONTENTS; Aldehydes

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1. INTRODUCTION

Aldehydes* are products of incomplete combustion of hydrocarbons and other organic materials. They are emitted into the atmosphere by exhaust from motor vehicles, incineration of wastes, and combustion of fuels (natural gas, fuel oils, and coal). Furthermore, aldehydes are formed from the photochemical reactions between nitrogen oxides and certain hydrocarbons, which are also emitted from the sources mentioned above. Thus, the ambient air is continually being polluted by aldehydes from emission sources and from atmospheric photochemical reactions. Moreover, aldehydes themselves can undergo photochemical reactions yielding oxidants (including ozone, peroxides, and peroxyacyl nitrate compounds) and carbon monoxide among the major products.

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*Aldehydes are organic compounds having a terminal carbonyl group. The general formula for aldehydes is R-CHO, where R represents either the hydrogen in the formula for formaldehyde or a hydrocarbon radical (such as CH_3- for acetaldehyde or CH_2=CH- for acrolein). In the aliphatic series the first two aldehydes, formaldehyde (C_1) and acetaldehyde (C_2), are gases at room temperature, while propionaldehyde (C_3) through hendecanal (C_{11}), are liquids. The lower members of the aliphatic series show a rapid decrease in water solubility, whereas caproaldehyde (C_6) and higher molecular weight aldehydes have practically no solubility.[73] The odors of aldehydes vary considerably. The lower aliphatic aldehydes (C_1 to C_7) have pungent, penetrating, unpleasant odors, while the higher aldehydes (C_8 to C_{14}) have generally pleasant odors and are used in making perfumes. The aldehydes above C_{14} have no appreciable odor.[73] Aldehydes with double bonds (unsaturated), such as acrolein and crotonaldehyde, tend to have a more penetrating and unpleasant odor than their corresponding members in the aliphatic series. The aromatic aldehydes generally have pleasing odors and are used in the perfume and food-flavoring industries.[73] Physical properties of aldehydes are given in Table 10 in the Appendix.

Aldehydes are very reactive compounds. They can easily undergo either reduction or oxidation reactions, as well as addition reactions (including self-polymerization) with many types of compounds. Detailed descriptions of these reactions can be found in most organic chemistry textbooks or encyclopedias.

At low concentrations the principal effect of aldehydes on both humans and animals is irritation of the eyes and upper respiratory tract. This is particularly true for the lower molecular weight aldehydes. The unsaturated aldehydes are several times more toxic than the saturated aldehydes.

In addition, aldehydes have been involved in plant damage. In some cases, the damage appears to be a result of oxidants produced by the photochemical reaction of aldehydes.

In the air pollution field major interest has been shown in two specific aldehydes--formaldehyde and acrolein. This is partly due to their effects on humans and to the fact that their concentrations are generally higher than those of other aldehydes present in the atmosphere. In addition, some reports indicate that formaldehyde and possibly acrolein may contribute to the odor and the eye irritation commonly experienced in polluted atmospheres. Thus, in addition to discussions of aldehydes in general, special attention has been given to formaldehyde and acrolein in this report.*

---

*Aldehyde concentration data in this report are calculated as formaldehyde. When necessary, conversion of reported concentration data to $\mu g/m^3$ was made by using the following factors: for aldehydes and formaldehyde, 1,200 $\mu g/m^3$ = 1 ppm; for acrolein, 2,500 $\mu g/m^3$ = 1 ppm.

2. EFFECTS

Despite the wide use of aldehydes and the consequent potential of aldehydes as air pollutants, comprehensive studies are not available as to their effect on humans, animals, plants, and materials. Particularly lacking are long-term studies with low concentrations of aldehydes. Much of the available information on toxicity of aldehydes pertains to the effects from single, acute exposures on animals.

2.1 Effects on Humans

2.1.1 Physiological Effects

The principal effect on humans of aldehyde vapors appears to be primary irritation of the eyes, respiratory tract, and skin.[52,70] The unsaturated (olefinic) and the halogenated aldehydes generally cause more noticeable irritation, than do the saturated aldehydes. Aromatic and heterocyclic aldehydes generally cause less irritation than saturated aldehydes. Furthermore, the irritant effect decreases with increasing molecular weight within a given aldehyde series. The toxicity of aldehydes appears to correspond with their irritant properties, although there are many exceptions. The toxicity of aldehydes generally decreases as the chain length increases.[70,182] However, the addition of a double bond greatly increases the toxicity of aldehydes. The lower, water-soluble aldehydes act chiefly on the eyes and upper respiratory tract, while the higher, less soluble aldehydes tend to penetrate more deeply into the respiratory tract and may affect the lungs.[168]

All aldehydes possess anesthetic properties.[70,168] However, an anesthetic effect, observed mainly in animal experiments,[184] is usually obscured by the more prominent irritant action on the eyes and upper respiratory tract. Moreover, the quantities of aldehydes that are generally tolerable by inhalation are so rapidly metabolized that no anesthetic symptoms are observable. The degree of anesthetic activity decreases with an increase in molecular weight of aliphatic aldehydes.[184]

Sensitization can occur by cutaneous contact with liquid solutions of aldehydes, but direct sensitization to the vapor of aldehydes is rare.[70]

In general, definite cumulative organic damage to tissues, other than that related to primary irritation or sensitization, is not commonly found.[70] The fact that aldehydes are readily metabolized in the body[217] probably accounts for the lack of a cumulative-type damage.

Table 10 in the Appendix lists some of the toxic effects of aldehydes on humans. Additional information on particular aldehydes can be found in the review by Fassett.[70]

2.1.1.1 Formaldehyde

The principal effect of formaldehyde vapors on humans appears to be irritation of the mucous membranes of the eyes, nose, and other portions of the upper respiratory tract.[47,70,76,83,133,168] Vapors may also cause skin irritation. Symptoms that have been observed from nonfatal exposures to formaldehyde include lacrimation, sneezing, coughing, dyspnea, a feeling of suffocation, rapid pulse, headache, weakness, fluctuations in body temperature, and, in sensitive persons, a dermatitis. Inhalation of high concentrations can cause laryngitis, bronchitis, and bronchopneumonia.[47] Reported responses of man to formaldehyde are summarized in Table 1.

Several reports indicate that irritation of the eyes and upper respiratory tract can first be detected at approximately 1,200 $\mu g/m^3$ (1 ppm) or below.[38,127,132,154] According to Fassett,[70] no discomfort is noted until 2,400 to 3,600 $\mu g/m^3$ (2 to 3 ppm), when a very mild tingling sensation may be detected in the eyes, nose, and posterior pharynx. At 4,800 to 6,000 $\mu g/m^3$ (4 to 5 ppm), the discomfort increases rapidly, and mild lacrimation may appear in some people. People generally cannot tolerate this concentration for more than 10 to 30 minutes. Concentrations of 12,000 $\mu g/m^3$ (10 ppm) cause profuse lacrimation in all people and can be endured for only a few minutes. In the concentration range of 12,000 to 24,000 $\mu g/m^3$ (10 to 20 ppm), breathing becomes difficult, coughing occurs, and irritation extends to the trachea. Upon removal from this exposure, lacrimation subsides promptly, but the nose and respiratory irritation may persist for an hour or more. The concentration at which serious inflammation of the bronchi and upper respiratory tract would occur is not known, but it has been estimated that exposure to 60,000 to

TABLE 1

REPORTED SENSORY RESPONSES OF MAN TO FORMALDEHYDE VAPORS

Concentration ($\mu g/m^3$)	Exposure Time	Response	Ref.
12		Eye irritation threshold	172
70		Odor threshold	127,128
80		Chronaximetric response threshold	127,128
98		Cortical reflex threshold	127,128
156-540		Irritant threshold	38
300-6,000		Irritant threshold	154
600		Odor threshold	195
1,000		Slight irritation	127
1,080-1,920		Irritant threshold	132
1,200		Odor threshold	70
2,400-3,600	8 hr	Tolerable; mild irritation of eyes, nose, and posterior pharynx	70
4,800-6,000	10-30 min	Intolerable to most people; mild lacrimation; very unpleasant	70
6,000		Throat irritation threshold	210
12,000	few min	Profuse lacrimation	70
24,000	15-30 sec	Lacrimation	33
24,000	30 sec	Irritation of nose and throat	33
24,000	1-2 min	Sneezing	33
60,000-120,000	5-10 min	May cause very serious damage	70

120,000 μg/m³ (50 to 100 ppm) for 5 to 10 minutes might cause serious damage.[70] (See Section 2.2.2.1 for a discussion of the effects of high concentrations of formaldehyde on experimental animals.)

Repeated exposures to formaldehyde vapors may result in chronic irritation of the eyes, nose, and other portions of the upper respiratory tract.[47, 168] Inflammation of the eyelids may also result from repeated exposures.[47]

Dermatitis and skin sensitization from cutaneous exposures to formaldehyde solutions and related derivatives are well documented. According to Fassett,[70] skin sensitization from exposure to formaldehyde vapors is rare; furthermore, no cases of authentic pulmonary sensitization have occurred. However, persons who have already developed an eczematous skin sensitization may have a skin reaction on exposure to formaldehyde vapors.

Melekhina[127,128] conducted studies to determine sensory threshold responses to formaldehyde. The odor threshold concentration for very sensitive people was 70 μg/m³. Reflex reactions threshold concentration for optical chronaxy tests was 80 μg/m³, and for dark adaptation the concentration was 98 μg/m³. Concentrations up to 2,500 μg/m³ produced no detectable changes in the frequency and rhythm of respiration.

All fatal poisonings reported from formaldehyde have resulted from ingestion.[76]

2.1.1.2 Acrolein

Acrolein vapors are highly toxic to humans. The vapor is extremely irritating to the eyes and respiratory tract.[70,80,143,168,185] Symptoms that have been reported from inhalation of acrolein include lacrimation, swelling of the eyelids, shortness of breath, pharyngitis, laryngitis, bronchitis, oppression in the chest, and somnolence.[48,133,143] The reported responses of man to acrolein vapors are summarized in Table 2.

Concentrations of acrolein as low as 625 μg/m^3 (0.25 ppm) can cause moderate irritation of the eyes and nose in 5 minutes.[185,219] Slight nasal irritation occurs from a 1-minute exposure to acrolein at 2,500 μg/m^3 (1 ppm). After 2 to 3 minutes at this concentration, eye irritation is quite noticeable and after 4 to 5 minutes it becomes practically intolerable. Sim and Pattle[182] reported that lacrimation occurred within 20 seconds at 1,880 μg/m^3 (0.805 ppm) and within 5 seconds at 2,800 μg/m^3 (1.22 ppm). Smith[185] reported that moderate eye and nasal irritation is produced from a 5-second exposure at 13,750 μg/m^3 (5.5 ppm), while a 20-second exposure is painful. Exposures to 54,500 μg/m^3 (21.8 ppm) are immediately intolerable to humans.[185] Pulmonary edema may develop from exposures to high concentrations of acrolein.[48] Sax[168] reports that inhalation

TABLE 2

REPORTED SENSORY RESPONSES OF MAN TO ACROLEIN VAPORS

Concentration ($\mu g/m^3$)	Exposure Time	Response	Ref.
525		Odor threshold	111
600		Dark adaptation response threshold	141
625	5 min	Moderate irritation	185
800		Odor threshold	141
1,500		Respiratory rhythm and wave amplitude response threshold	141
1,750		Chronaximetric response threshold	141
1,880	20 sec	Lacrimation	182
2,500	1 min	Slight nasal irritation	185
2,500	2-3 min	Slight nasal irritation and moderate eye irritation	185
2,500	2-3 min	Eye and nose irritation	80
2,500	4-5 min	Moderate nasal irritation; practically intolerable eye irritation	185
2,800	5 sec	Lacrimation	182
4,500	1 min	Slight eye irritation	185
4,500	3-4 min	Profuse lacrimation; practically intolerable	185
13,750	5 sec	Slight odor; moderate eye and nasal irritation	185
13,750	20 sec	Painful eye and nasal irritation	185
13,750	60 sec	Marked lacrimation; vapor practically intolerable	185
54,500	Immediate	Intolerable	185
375,000	10 min	Lethal	143

of acrolein may cause an asthmatic reaction.

No cases of chronic toxicity are known.[48,70,185] However, repeated contact with the skin may produce chronic irritation and a dermatitis. Acrolein is reported to be a weak sensitizer.[168]

Plotnikova[141] studied some of the sensory responses of man to acrolein. The threshold concentration of acrolein on the reflex action and optical chronaxy was determined to be 1,750 $\mu g/m^3$, while 1,500 $\mu g/m^3$ was the threshold for respiratory rhythm and wave amplitude. Threshold response to dark adaptation was established at 600 $\mu g/m^3$, which was below the measured odor threshold of 800 $\mu g/m^3$.

There was one reported case of fatal poisoning from acrolein inhalation of 375,000 $\mu g/m^3$ (150 ppm) for 10 minutes.[143]

2.1.2 Annoyance Effects

Several studies have been made to determine the contribution of aldehydes to the odor and eye irritation resulting from air pollution. Although present studies indicate that these effects are not entirely the result of atmospheric aldehydes, the aldehydes seem to contribute in some degree to these effects.

2.1.2.1 Odor

The reported odor threshold values for formaldehyde and acrolein appear to be in the range of 70 to 1,200 $\mu g/m^3$

(0.06 to 0.2 ppm) and 525 to 800 μg/m³ (0.2 to 0.3 ppm), respectively (see Sections 2.1.1.1 and 2.1.1.2). Three separate studies[65,155,216] on odors in diesel exhaust (see Table 3) indicate that the odor threshold for aldehydes (measured by modified Schiff reagents) is in the range of 600 to 14,400 μg/m³ (0.5 to 12 ppm). Although these studies show a correlation between odor intensity and aldehyde concentration, the relationships differ somewhat. Linnell and Scott[114] found that the concentration of formaldehyde and acrolein in diesel exhaust, when diluted to the odor threshold, was too low to be a major contributing factor to the odor of diesel exhaust. In contrast, Fracchia et al.[77] measured the concentration of certain aldehydes in automobile exhaust and concluded that the odor might be due to an additive effect of all the concentrations of these aldehydes.

2.1.2.2 Eye Irritation

"Eye irritation is by far the most noticeable obnoxious symptom of smog as far as the public is concerned," according to Hamming and MacPhee[84].

In 1960, Renzetti and Bryan[147] found a good correlation between intensity of eye irritation and the concentration of total aldehydes (measured by bisulfite method) and of formaldehyde in the Los Angeles smog. Renzetti and Schuck[148] studied the photooxidation of hydrocarbons and found that formaldehyde and acrolein accounted for the majority of the eye irritation

TABLE 3

REPORTED CORRELATION BETWEEN ALDEHYDE CONCENTRATION AND ODOR INTENSITY IN DIESEL EXHAUST

Odor Unit	Odor Intensity	Aldehyde Concentration ($\mu g/m^3$)* Reference 155	Reference 65	Reference 216
0	No odor			8,520
1	Very faint	624	1,140	14,400
2	Faint	6,600	4,800	25,200
3	Easily noticeable	57,600	21,600	42,000
4	Strong	504,000	96,000	72,000
5	Very strong			120,000

*Calculated as formaldehyde.

produced by photochemical products. However, the concentration of these aldehydes needed to produce eye irritation in these experiments was well in excess of measured atmospheric concentrations. Several other compounds were thought to explain eye irritation,[172,193] but most have not proved to be of major importance, with the exception of peroxyacyl nitrate compounds. Recently, Schuck et al.[172] found in simulated atmosphere experiments that the linear correlation between eye irritation intensity and formaldehyde concentration does not hold at concentrations below 360 μg/m³ (0.3 ppm). In fact, concentrations of 60 μg/m³ (0.05 ppm) and 600 μg/m³ (0.5 ppm) produce the same irritation intensity in most of the people exposed. Furthermore, it was found that the human eye can detect and respond to as little as 12 μg/m³ (0.01 ppm) formaldehyde. Thus, these authors predicted that the concentration of formaldehyde and peroxyacetyl nitrate in polluted air can account for most of the detected eye irritation.

Recent data[174] of interest in relation to these findings are the ambient air concentrations in the Los Angeles area: for aliphatic aldehydes, 196.8 μg/m³; for formaldehyde, 163.2 μg/m³; and for acrolein, 27 μg/m³.

2.2 Effects on Animals

2.2.1 Commercial and Domestic Animals

No cases were found of injury or death of domestic or commercial animals from environmental exposure to aldehydes.

2.2.2 Experimental Animals

The effect of aldehyde vapors on animals is similar to that found in humans (see discussion in Section 2.1). The principal effect observed is primary irritation to the mucous membranes of the eyes and the upper respiratory tract, particularly the nose and throat. Exposure to high concentrations of aldehydes may cause injury to the lungs as well.

Fassett[70] has summarized the reported toxicity data on exposures of animals to aldehydes; part of his summary (toxicity from inhalation of aldehydes) is given in Table 11 in the Appendix.

2.2.2.1 Formaldehyde

Studies indicate that high concentrations of formaldehyde, besides causing prompt and severe irritation of the eyes and respiratory tract, may cause injury to the lungs and other organs. Thus, Skog,[183] exposing rats (in groups of eight) to high concentrations of formaldehyde (e.g., 960,000 $\mu g/m^3$ or 800 ppm), found hemorrhages and pulmonary edema and signs of hypercrinemia and perivascular edema in the liver and kidneys. Salem and Cullumbine[156] exposed groups of 50 mice, 20 guinea pigs, and 5 rabbits simultaneously to formaldehyde (19,000 $\mu g/m^3$) and other aldehydes for periods up to 10 hours. Autopsy of the animals killed by the vapors showed expanded edematous and hemorrhagic lungs, fluid in the pleural and peritoneal cavities, consolidation, distended alveoli, and ruptured alveolar septa. In addition, Murphy et al.[136] found in a group of eight male rats that the alkaline phosphatase activity in the liver was increased after the rats inhaled 4,200 μg/m^3 (35 ppm) formaldehyde for 18 hours.

The response of lung functions has been studied with normal and tracheotomized animals.[25,26,62,135] The responses to formaldehyde inhalations were an increase in flow resistance and in tidal volume and a decrease in the respiratory rate. According to Amdur,[25] the responses of tracheotomized animals were similar, but much greater, than those observed with the normal animals. The author attributed this result to the fact that the tracheal cannula prevents removal of the formaldehyde by the nasal and upper airway passages. In contrast, Davis et al.[62] recently reported that in comparison with normal animals, tracheotomized animals showed an increase in respiration rate accompanied by a decrease in tidal volume. These findings were ascribed to the fact that the receptors for the responses observed in the normal animals are in the upper airway (i.e., larynx and above), which was blocked in the tracheotomized animals. Exposure of the larynx and the nasopharynx of the tracheotomized animals elicited the responses shown by normal animals.

Investigators have demonstrated that formaldehyde can cause cessation of ciliary activity.[55,59,101] In one study,[59] low doses of formaldehyde, such as 3,600 μg/m^3 (3ppm) for

50 seconds or 600 $\mu g/m^3$ (0.5 ppm) for 150 seconds, caused cessation of ciliary beat in anesthetized, tracheotomized rats.

In a Russian study, Gofmekler[79] investigated the effects of continuous exposure of pregnant rats to concentrations of formaldehyde of 12 and 1,000 $\mu g/m^3$. Two groups of 12 female rats were exposed, each group to one concentration. Another group of 12 pregnant rats was used for control. The two groups of test rats were also exposed to formaldehyde vapors 10 to 15 days prior to impregnation. Significant results were subsequently found. The mean duration of pregnancy was prolonged by 14 to 15 percent from exposure to both concentrations. A regular decrease in the number of fetuses per female was found with the higher concentration of formaldehyde. Furthermore, the exposure to formaldehyde appeared to cause an increase in the weight of the thymus, heart, kidneys, and adrenals in the offspring. This effect, the author concluded, was apparently a compensatory reaction to unfavorable environmental conditions. On the other hand, the lungs and liver, the organs which are directly affected by formaldehyde, showed a decrease in weight following the aldehyde exposure.

2.2.2.2 Acrolein

Acrolein, as most other unsaturated aldehydes, is much more irritating and toxic than the aliphatic aldehydes.[70]

Thus, the lethal concentration (LD_{50}) of acrolein for rats is approximately one-third that for formaldehyde and approximately 0.005 that for propionaldehyde, its aliphatic counterpart.

The damage to the lungs and other organs described for formaldehyde applies equally to acrolein.[156,183] Murphy et al.[136] reported an increase in alkaline phosphatase activity in the liver from exposure to 5,250 μg/m³ (2.1 ppm) acrolein for 40 hours.

Murphy et al.[137] exposed guinea pigs (group of 10) to 1,500 μg/m³ (0.6 ppm) acrolein to determine respiratory responses. The results indicate that acrolein vapors increase the flow resistance and tidal volume, while decreasing the respiration rate. The magnitude of these effects increases with high concentrations of acrolein. The effects were found to be reversible upon return to clean air. Results from the administration of certain drugs indicated that the acrolein-induced increase in respiratory resistance is probably due to bronchoconstriction mediated through reflex cholinergic stimulation.

Gusev et al.[81] continually exposed groups of 10 rats each to 150, 510, and 1,520 μg/m³ of acrolein in air over a period of several weeks. The rats exposed to the 1,520 μg/m³ concentration for 24 days showed a loss of weight, changes in conditioned reflex activity, a decrease in cholinesterase activity of whole blood, a fall of coproporphyrin excretion in the urine, and an increase in the number of luminescent leukocytes in the blood. Exposures to 150 μg/m^3 acrolein for 61 days caused only a rise in the number of luminescent leukocytes in the blood.

Catilina et al.[43] exposed rats to 500,000 μg/m^3 (200 ppm) acrolein for 10 minutes once a week for 8 weeks. Lung damage was still observable 6 months after the exposure period ended.

2.2.2.3 Synergistic Effects

Several investigators have found that the effects of aldehydes on animals can be significantly increased in the presence of an aerosol. LaBelle et al.[105] exposed mice to constant concentrations of formaldehyde and acrolein (15,000 μg/m^3) in the presence and absence of aerosols. Nine different substances were used as aerosols, including solids and liquids. The time for 50 percent survival of the mice (minimum of 6 mice in 12 groups) was measured. The results are shown in Table 4. Significant increases in death rates were found for both formaldehyde and acrolein with some of the aerosols. These investigators also noted that the active aerosols increased the pulmonary edema caused by formaldehyde and acrolein.

Amdur[24,26] investigated the response of guinea pigs to inhalation of formaldehyde in the presence and absence of

TABLE 4

SURVIVAL TIME OF MICE EXPOSED TO FORMALDEHYDE AND ACROLEIN IN PRESENCE OF AEROSOLS[105]

	Formaldehyde			Acrolein		
Aerosol (Size, μ)	Aerosol Concentration (μg/liter)	ST$_{50}$[a] (min)	Significance[b]	Aerosol Concentration (μg/liter)	ST$_{50}$[a] (min)	Significance[b]
None		147			87	
Triethylene glycol (1.8)	2210	71	++	380	73	0
Ethylene glycol (2.0)	2920	168	0	500	106	0
Mineral oil (2.1)	1420	72	++	240	69	+
Glycerin (2.0)	1280	114	++	220	94	0
Sodium chloride (2.6)	2320	114	+	390	71	+
Dicalite (3.3)	420	118	+	70	91	0
Celite[c] (2.9)	360	102	++	60	99	0
Attapulgus clay[d] (3.3)	960	157	0	160	78	0
Santocel CF[e] (2.7)	310	145	0	50	65	+

[a] Time for 50 percent survival of mice.

[b] 0 = no significance, + = significant, ++ = highly significant.

[c] Diatomaceous earth.

[d] Highly absorptive clay.

[e] Commercial silica gel.

sodium chloride aerosols (approximately 0.04 μ[*] in diameter). The concentration of formaldehyde varied from approximately 84 to 56,400 $\mu g/m^3$ (0.07 to 47 ppm), with and without the presence of 10,000 $\mu g/m^3$ of sodium chloride aerosol. Statistically significant increases in "respiratory work" as a result of the aerosol were found when the formaldehyde concentration was 360 $\mu g/m^3$ (0.3 ppm) or above. Moreover, compared with the pure vapor, the formaldehyde-aerosol mixture delayed the recovery after discontinuation of the exposure. Further experiments indicated that as the amount of aerosol was increased from 0 to 3,000 $\mu g/m^3$, 10,000 $\mu g/m^3$, and 30,000 $\mu g/m^3$, an increase in flow resistance was also observed. The authors concluded that sodium chloride aerosol, which is itself inert, can cause the response to formaldehyde to be potentiated (the higher the concentration of aerosol, the greater the effect), and also prolong the response, compared with the response to the pure vapor.

2.3 Effects on Plants

There is very little information available on the effects of atmospheric aldehydes on plants. Moreover, most of the data has been derived from studies of product mixtures obtained from the irradiation of aldehydes, hydrocarbons, or hydrocarbon-nitrogen oxide mixtures. While these resulting mixtures contain some aldehydes, they also contain other compounds, some unidentified, which may be phytotoxicants. Thus, in these studies, the role of aldehydes in plant damage may well be obscured by the presence of other compounds.

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[*] μ = micron.

Brennan _et al._[39] reported in 1964 that the damage to foliage of Snowstorm petunias grown in a greenhouse was related to the high aldehyde content of the ambient air. Leaf damage occurred when the aldehyde content exceeded 240 $\mu g/m^3$ (0.2 ppm) for 2 hours or 360 $\mu g/m^3$ (0.3 ppm) for 1 hour. Injury, which appeared within a day or two after the exposure, was characterized by symptoms of necrotic banding of the upper leaf surface and glazing of the lower leaf surface. Although the damage was similar to that found with photochemically produced pollutants or "oxidant" type phytotoxicants in the atmosphere,* the level of "oxidants" in the atmosphere was below normal on the days that the aldehyde content was sufficient to cause plant damage.

However, these data do not prove that aldehydes directly attacked the plant tissue. Other explanations might be that there is a synergistic effect with a high concentration of aldehydes or that aldehydes react photochemically to yield phytotoxicant products that may be undetected by the methods of analysis used. Indeed, several studies have shown that irradiation of certain aldehydes will cause formation of phytotoxicant compounds other than the original aldehydes.[10, 23,88,193,199] Stephens et al.[193] found that irradiated aldehydes yielded phytotoxicants that caused oxidant-type damage to petunias and bean plants. Hindawi and Altshuller[88] irradiated propionaldehyde and nitrogen oxide mixtures and concluded that irradiation of propionaldehyde in air will definitely cause appreciable plant damage to tobacco wrapper, pinto bean leaves at various stages of development, and petunias. In contrast, irradiated formaldehyde-nitrogen oxide mixtures caused no observable plant damage.[23,88] Recent studies indicate that irradiation of most aldehyde-nitrogen oxide mixtures produces PAN*-type products, among other compounds.[10] (See further discussion under Atmospheric Photochemical Reactions, Section 3.4.1).

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*A similar type of plant damage was shown by Taylor _et al._[200] from polluted ambient air in California and from irradiated mixtures of nitrogen dioxide and hexene. Stephens _et al._[193] induced similar damage to petunias with irradiated mixtures of (a) automobile exhaust, (b) olefins and nitrogen oxide, (c) olefin and ozone, and (d) aldehydes.

2.3.1 Formaldehyde

Haagen-Smit et al.[82] found no evidence of damage to alfalfa after 2 hours' exposure to 2,400 μg/m³ (2 ppm) of formaldehyde, but did find atypical alfalfa damage after 5 hours at 8,400 μg/m³ (7 ppm) of formaldehyde. Hindawi and

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*PAN: peroxyacetyl nitrates.

Altshuller[88] found no damage to pinto beans, tobacco wrapper, and petunias from exposure to mixtures of formaldehyde-nitrogen oxide that had been irradiated for 4 hours.

2.3.2 Acrolein

Data indicate that acrolein may be a phytotoxicant. Haagen-Smit *et al.*[82] reported oxidant-type damage to alfalfa grown in a greenhouse and exposed to 250 μg/m³ (0.1 ppm) of acrolein for 9 hours. Similar damage, along with atypical leaf damage, was observed with spinach, endive, and beets exposed to acrolein vapor concentrations of 3,000 μg/m³ (1.2 ppm) for 4.5 hours or 1,500 μg/m³ (0.6 ppm) for 3 hours. Darley *et al.*[61] found oxidant-type damage to 14-day-old pinto bean plants exposed to approximately 5,000 μg/m³ (2 ppm) of acrolein for four successive 35-minute periods. However, Hindawi and Altshuller[88] observed that 2,500 μg/m³ (1 ppm) of acrolein, produced from the irradiation of 1,3-butadiene-nitrogen oxide mixture, caused no damage to petunia, pinto bean, or tobacco wrapper.

2.4 Effects on Materials

There are no data available to indicate the effect of atmospheric concentration of aldehydes on materials.

2.5 Environmental Air Standards

The American Conference of Governmental Industrial Hygienists has adopted 8-hour threshold limit values for occupational exposure to several aldehydes (see Table 5).[204]

TABLE 5

EIGHT-HOUR DAY THRESHOLD LIMIT VALUES, AMERICAN CONFERENCE OF GOVERNMENTAL INDUSTRIAL HYGIENISTS, 1967[204]

Aldehyde	ppm	$\mu g/m^3$
Acetaldehyde	200	360,000
Acrolein	0.1	250
Chloroacetaldehyde	1[a]	3,000[a]
Crotonaldehyde	2	6,000
Formaldehyde	5	6,000
Furfural (skin)[b]	5	20,000

[a] This is a "ceiling" value, which should not be exceeded at any time.

[b] Cutaneous exposure can significantly contribute to harmful effects.

In 1968, the American Industrial Hygiene Association[52] recommended ambient air quality values for certain aldehydes to prevent sensory irritation of any form, as follows:

Formaldehyde	120 $\mu g/m^3$	0.1 ppm
Acrolein	25 $\mu g/m^3$	0.01 ppm
Total aldehydes (as formaldehyde)	240 $\mu g/m^3$	0.2 ppm

West Germany and Russia have established ambient air quality standards for acetaldehyde, acrolein, formaldehyde, and furfural.[197] These standards are summarized in Table 6.

TABLE 6

AMBIENT AIR QUALITY STANDARDS[197]

Aldehyde	Country	Basic Standard		Permissible Standard[a]	
		$\mu g/m^3$	Averaging Time	$\mu g/m^3$	Averaging Time
Acetaldehyde	West Germany	4,000	30 min	12,000	30 min
	Russia			10	20 min
Acrolein	West Germany	10	30 min	25	30 min
	Russia	100	24 hr	300	20 min
Formaldehyde	West Germany	36	30 min	84	30 min
	Russia	14.4	24 hr	42	20 min
	Czechoslovakia	18	24 hr	60	30 min
Furfural	West Germany	80	30 min	250	30 min
	Russia	50	24 hr	50	20 min

[a] Not more than once every 4 hours.

3. SOURCES

Aldehydes that pollute the atmosphere result from two main sources: (1) incomplete combustion of organic compounds and (2) atmospheric photochemical reactions involving mainly hydrocarbons and nitrogen oxides. Thus, the highest concentrations of atmospheric aldehydes are expected to be in the populated areas where combustion of fuels and motor-vehicle exhaust emit significant amounts of aldehydes and compounds that form aldehydes through photooxidation.

Emission data reported for certain towns, cities, and counties of the United States are summarized in Table 12 in the Appendix. The highest reported value for a city is 1,139 tons of aldehydes per year for the city of St. Louis. Emission of aldehydes from various sources as reported by certain cities and counties is shown in Table 7. These data indicate that emission of aldehydes to the atmosphere is primarily due to automobile exhaust, followed by burning of wastes and combustion of fuel.

3.1 Natural Occurrence

Natural sources of aldehydes do not appear to be important contributors to air pollution. Acetaldehyde is found in apples and as a by-product of alcoholic fermentation processes.[73] Other lower aliphatic aldehydes are not found in significant quantities in natural products. Olefin and aromatic aldehydes are present in some of the essential oils

TABLE 7. SUMMARY OF EMISSIONS OF ALDEHYDES, 1963[97]
(tons/year)

Source	City of St. Louis, Mo.	St. Louis County, Mo.[a]	St. Charles County, Mo.	Jefferson County, Mo.	St. Clair County, Ill	Madison County, Ill.	Monroe County, Ill.	Total	Percent
Road vehicles (gasoline)	610	525	39	44	146	134	10	1,508	40.8
(diesel)	45	10	b	b	3	2	b	60	1.6
Railroads and vessels	55	8	14	9	75	23	12	196	5.3
Fuel use (residential)	117	148	10	11	36	34	2	358	9.7
(industrial)	23	19	b	10	20	135		207	5.6
Fossil fuel steam electric plants	b	7			1	8		16	0.4
Other fuel use	13	10	b	b	2	3	b	28	0.8
Municipal incineration	39							39	1.0
Residential incineration	16	9						25	0.7
Industrial and commercial incineration	63	8	b	6	7	2	b	86	2.3
Open burning (dumps)				110	371	53	30	546	15.3
(on-site)	158	81	26	16	150	140	9	580	15.7
Aircraft (jet piston, turboprop)		28						28	0.8
Total	1,139	853	89	206	811	534	63	3,695	100.0

[a] Excluding city of St. Louis
[b] Less than 0.5 tons/year.

in fruits and plants. These include citronellal, in rose oil; citral, in oil of lemongrass; bensaldehyde, in oil of bitter almonds; cinnamaldehyde, in oil of cinnamon; anisaldehyde, in anise; and vanillin, in the vanilla bean.

3.2 Production Sources

Aldehydes are commercially manufactured by various processes, depending on the particular aldehyde. In general, they are prepared via oxidation reactions of hydrocarbons, hydroformylation of alkenes, dehydrogenation of alcohols, and addition reactions between aldehydes and other compounds.

The commercial manufacture of formaldehyde and acrolein is discussed in the following sections. Formaldehyde is a very important chemical and is produced in the largest quantities by far of all the aldehydes.

3.2.1 Formaldehyde Manufacture

Formaldehyde production in the United States has generally shown a steady growth since manufacture was first begun.[210,211] The United States production figures for formaldehyde for 1958 through 1968 (see Table 13, Appendix) illustrate this general growth to over 4 billion pounds in 1968. The data also indicate that most of the formaldehyde is consumed by the manufacturer. A list of the major manufacturers of aldehydes in the United States is given in Table 14 in the Appendix.

Industrial plants producing formaldehyde may be local sources of atmospheric pollution. Levaggi and Feldstein[113] found that approximately 3,000,000 μg/m³ (2,580 ppm) of formaldehyde and 290,000 μg/m³ (162 ppm) of acetaldehyde were in the effluent from a formaldehyde plant.

Most formaldehyde is manufactured from oxidation of methanol.[211] However, a small amount (14 percent of total production in the United States in 1960) is produced by the partial oxidation of gaseous hydrocarbons.

The methanol process involves passing a methanol vapor air mixture over a catalyst. Some manufacturers use a silver or copper catalyst at 450° to 650°C, while others use an iron-molybdenum oxide catalyst at 300° to 400°C. With the metallic catalyst, the alcohol-air mixture is rich in methanol and yields a methanol solution of formaldehyde. With the oxide as catalyst, an alcohol-lean mixture is used which produces a substantially methanol-free solution. Generally, two main reactions can occur--dehydrogenation and oxidation, which are represented by Equations 1 and 2, respectively:

$$CH_3OH \xrightarrow{\text{cat.}} HCHO + H_2 \qquad \text{(Equation 1)}$$

$$CH_3OH + \tfrac{1}{2}O_2 \xrightarrow{\text{cat.}} HCHO + H_2O \qquad \text{(Equation 2)}$$

In the metal-catalyzed process, the main reaction is dehydrogenation (Equation 1), with little if any formaldehyde formed via oxidation. The oxide-catalyzed process, in contrast, proceeds mainly via the oxidation reaction. Product vapors are passed from the converter to a series of contracurrent water scrubbers to cool the gases and dissolve the formaldehyde. Excess methanol is removed by fractional distillation.

In the hydrocarbon oxidation process, the reaction can occur with or without a catalyst in the presence of air or oxygen. The main disadvantage of this process is the formation of numerous oxidation products, including other aldehydes, alcohols, and organic acids. Thus, the recovery of the important products requires specific and complicated separation procedures. In fact, this process is used primarily for manufacture of other products, with formaldehyde recovered as a by-product.

3.2.2 Acrolein Manufacture

Acrolein is produced by two manufacturers in the United States (see Table 14 in the Appendix). Data on the production and sales of acrolein are not available. The commercial methods of preparation are discussed below. No data were found on the emission of acrolein or other aldehydes from these processes.

Acrolein is generally commercially produced either by the direct oxidation of propylene or by the cross-condensation of acetaldehyde with formaldehyde.[80,185]

In the oxidation of propylene the hydrocarbon vapor is passed over a catalyst at 300° to 350°C in the presence of air or oxygen. The catalysts are generally metallic oxides such as cuprous oxide, oxide mixtures of bismuth and molybdenum, oxide mixtures of cobalt and molybdenum, oxides of antimony plus other metals, and various other combinations. The general reaction is given in Equation 3.

$$CH_2{=}CH{-}CH_3 + O_2 \xrightarrow{\text{cat.}} CH_2{=}CH{-}CHO + H_2O \quad \text{(Equation 3)}$$

The principal by-products are water and carbon dioxide from the undesired complete oxidation of the propylene. Excess propylene is used to avoid complete combustion. Other products that are formed in minor amounts include formaldehyde, acetaldehyde, propionaldehyde, and acetone. The formed acrolein passes along with the other by-product gases through a cooler and then through an aqueous scrubber. Fractional distillation is used to separate the acrolein from the water and other water-soluble products.

The second method, cross-condensation of acetaldehyde with formaldehyde, is also a vapor phase reaction in which the two reactants are passed over a catalyst at 300° to 350°C.

The catalysts used are generally associated with promotion of dehydration reactions and include lithium phosphate on activated alumina and sodium silicate on silica gel. The reaction is represented in Equation 4.

$$CH_2O + CH_3CHO \xrightarrow{\text{cat.}} CH_2{=}CH{-}CHO + H_2O \quad \text{(Equation 4)}$$

Acetaldehyde is most frequently used in excess since formaldehyde is the more difficult component to recover of the two unreacted components. The by-products of the reaction include crotonaldehyde, methanol, propionaldehyde, carbon dioxide, carbon monoxide, hydrogen, and tar. The tar remains on the catalyst and thus decreases the efficiency of the conversion. The catalyst is reactivated with air and steam at 400°C. The effluent gas containing acrolein leaves the converter, passes through a cooler, and subsequently through a water scrubber to remove the noncondensables. The acrolein is separated from the aqueous mixture by fractional distillation.

3.3 Product Sources

Aldehydes have a wide variety of uses in numerous industries, such as the chemical, rubber, tanning, paper, perfume, and food industries. The major use is as an intermediate in the synthesis of organic compounds, including alcohols, carboxylic acids, dyes, and medicinals. Uses of formaldehyde and acrolein are discussed in further detail in the following sections.

3.3.1 Formaldehyde Products

Formaldehyde is commercially marketed chiefly in the form of an aqueous solution containing 36 to 50 percent by weight of formaldehyde. Dilution is necessary since pure formaldehyde will polymerize readily on standing. Formaldehyde is also sold in other forms, including paraformaldehyde (polymeric hydrate), trioxane (a cyclic polymer), hexamethylenetetramine, and various alcoholic solutions.

Its chemical and physical properties, as well as its low price, have made formaldehyde a widely used chemical. Formaldehyde has immense utility as illustrated by its use as a resinifying agent, synthetic agent, hardening agent, stiffening agent, tanning agent, disinfectant, bactericide, and preservative.[210,211] The consumption of formaldehyde by uses is shown in Table 15 in the Appendix. Synthetic resins account for over half of the consumption.

Formaldehyde has numerous applications in a variety of fields; these include:[210,211]

Resins. In addition to the resins listed in Table 15 in the Appendix, formaldehyde is used to make resins from aniline, aromatic hydrocarbons, ketones, urethane, and other compounds. These resins find widespread applications in the electrical, automotive, building, chemical, and petroleum industries.

Agricultural Uses. The urea-formaldehyde concentrates are used for preparing slow-releasing nitrogen fertilizers and for preventing plant diseases by destruction or control of microorganisms.

Analysis. Small quantities of formaldehyde are used in the qualitative and quantitative analysis of chemical compounds.

Catalysts. Formaldehyde and its derivatives are used as catalysts and in the preparation of catalysts for the manufacture of hydrocarbons, alcohols, and resins.

Concrete, Plaster, and Related Products. Formaldehyde is employed as one of the addition agents to make concrete, plaster, and related products impermeable to liquids and grease.

Cosmetics. It is useful as an antiperspirant and as an antiseptic in dentifrices, mouthwashes, and germicidal and detergent soaps.

Deodorants. It is used as an air deodorant in public places and the home and for deodorizing numerous products.

Disinfectants and Fumigants. Formaldehyde can destroy bacteria, fungi, molds, and yeasts and is therefore used in disinfectant applications.

Dyes and Dyehouse Chemicals. It is employed in the synthesis of dyes, stripping agents, and various specialty chemicals of the dye industry.

Embalming Fluids and Preservatives. It is an ingredient in embalming fluids and in preservatives for waxes, polishes, adhesives, fats, oils, starches, ferns, flowers, textiles, anatomical specimens, etc.

Explosives. Formaldehyde is used in synthesis of explosives such as pentaerythritol tetranitrate.

Fireproofing Material. It is an ingredient in manufacturing several fireproofing compositions applied to fabrics.

Fuels. Numerous solid fuels contain formaldehyde polymers.

Hydrocarbon Products. Formaldehyde is used in oil-well operations, in refining of hydrocarbons, and for stabilization in gasoline fuels.

Insecticides. Certain insecticidal solutions for killing flies, mosquitoes, moths, and other insects contain formaldehyde.

Leather. Formaldehyde is used as tanning agent of white washable leather, hides, and hairs; also used as a preservative and disinfectant of leather products.

Medicinals. It is used in synthesis of numerous medicinal preparations, including vitamins and vaccines, and as a detoxifying agent.

Metals. Formaldehyde and its derivatives are used as pickling addition agents, for control of corrosion of metals by hydrogen sulfide, in preparation of mirrors, in electroplating, and as metal sequestering agents.

Paper. Formaldehyde is used for improving the wet-strength, water-resistance, shrink-resistance, and grease-resistance of paper, coated papers, and paper products.

Photographic Materials. It is used to harden and insolubilize film and in reducing silver salts.

Proteins. It is employed in production of protein fibers.

Rubber. It is used in vulcanization and modification of natural and synthetic rubber, and in the synthesis of rubber accelerators and antioxidants.

Solvents and Plasticizers. Formaldehyde is used in synthesis of polyhydroxy compounds, formals, and other methylene derivatives for solvents and plasticizers.

Starch. It is used to modify properties of starches.

Surface-Active Agents. It is employed in synthesis of several surface-active compounds.

Textiles. It is used to make natural and synthetic fibers crease-resistant, crush-proof, flame-resistant, shrink-proof, etc.

Wood. Formaldehyde is an ingredient in wood preservatives.

3.3.2 Acrolein Products

Acrolein is consumed in large quantities in the manufacture of several derivatives, including 1,2,6-hexanetriol, hydroxy adipaldehyde, and glutaraldehyde.[80] One of the largest single uses of acrolein is in the synthesis of methionine, an amino acid used to fortify chicken and dog foods. Acrolein is also an ingredient in synthetic resins.

3.4 Other Sources

Significant amounts of atmospheric aldehydes, particularly formaldehyde, are a result of photooxidation of unsaturated hydrocarbon pollutants. In addition, some important contributing sources of aldehyde air pollution are the burning or heating of organic compounds. These sources include mobile combustion (automobiles, diesel vehicles, and aircraft), stationary combustion (units that burn coal, oil, natural gas, or waste materials), and noncombustion sources (e.g., chemical oxidation processes, and drying and baking in ovens).

3.4.1 Atmospheric Photochemical Reactions

Atmospheric photochemical reactions may be major contributors to aldehyde air pollution in some areas. The importance of this source does, of course, depend upon such factors as concentration of atmospheric reactants and amount of sunlight. Furthermore, the presence of atmospheric aldehydes may also contribute to production of other photochemical pollutants by (1) photochemical reactions of the aldehydes to form new products, and (2) interaction of an aldehyde or its photochemical products with other atmospheric pollutants to yield additional products. Thus, the photochemical aspects of air pollution are quite complicated and not yet thoroughly understood. Reviews on the subject have been prepared by Stern,[195] Altshuller and Bufalini,[11] Wayne,[213] and Leighton.[110]

3.4.1.1 Photochemical Formation of Aldehydes

Aldehydes are major products in the photooxidation of reactive hydrocarbons. This includes such systems as olefin-nitrogen oxides,[12,23,169,170,181,191,192,193,205] aromatic-nitrogen oxides,[23,103,169,192] olefin-ozone,[11,13,175] olefin-molecular oxygen,[57,157,158] and aldehyde-nitrogen oxides.[23] Formaldehyde is produced in substantial amounts by the photooxidation of almost all olefins and aromatic hydrocarbons,[8,23,57,169] and is found as a product of photooxidation of higher aldehydes.[8,23] Acrolein is derived mainly from photooxidation of diolefins, such as 1,3-butadiene.[169,180,193] A summary of some of the reported yields of formaldehyde, acrolein, and "total" aldehydes from photooxidation of hydrocarbon-nitrogen oxide mixtures is given in Table 16 in the Appendix.

Thus, atmospheric photochemical reactions may be a major contributor to formation of aldehydes in the atmosphere when it is contaminated with large amounts of nitrogen oxides and reactive hydrocarbons. Altshuller[10] found that an air sample taken in Los Angeles, Calif., between 7 and 8 a.m. contained approximately 120 $\mu g/m^3$ (0.1 ppm) of formaldehyde. Upon irradiating this sample in sunlight for several hours, the formaldehyde increased over threefold to 420 $\mu g/m^3$ (0.35 ppm). The final concentration of "aldehydes" (calculated as formaldehyde) was approximately 600 $\mu g/m^3$ (0.5 ppm). In a similar experiment, Sigsby et al.[180] found that irradiation of diluted automobile exhaust (which contained approximately 120 $\mu g/m^3$ (0.1 ppm) of aldehydes) caused the aldehyde level to increase by a factor of five. Formaldehyde accounted for approximately 60 percent of the total aldehydes in the irradiated mixture.

3.4.1.2 Products from Photooxidation of Aldehydes

The concentration of aldehydes in photochemical reactions appears to be important in determining the products. Thus, while peroxyacids and diacetyl peroxides are the major products from photooxidation of high concentrations of aldehydes,[42,123,124,125] these products have not been produced from photooxidation of atmospheric concentrations of aldehydes.

In general, the products of photooxidation at low partial pressures of aldehydes in the presence of nitrogen oxides are carbon monoxide, lower aldehydes, nitrates, and oxidants.[8,10,14,15,18,145,146] The oxidants produced include ozone and alkyl hydroperoxide (hydrogen peroxide in the case of formaldehyde). In addition, peroxyacyl nitrate compounds are found in small amounts.[10] Hence, the products in some cases are reactive species that contribute to eye irritation and plant damage.

Furthermore, the photochemical products from aldehydes can react with olefins and aromatic hydrocarbons.[19] Although the rates of these reactions are less than the photochemical olefin-nitrogen oxide reactions, the rates are significant when considering photochemical atmospheric reactions.

The reactivity of aldehydes appears to be slightly greater than that of ethylene, similar to the reactivity of substituted aromatic hydrocarbons, but less than that of olefins and diolefins.[8,23]

3.4.2 Mobile Combustion Sources

A major source of aldehyde pollution may be the emissions from motor vehicles. Conlee *et al.*[53] determined the contribution of motor vehicle emissions to air pollution by comparing the concentration of pollutants at the entrance and exit of the Sumner Tunnel, a one-way, 1.1-mile-long tunnel in Boston, Mass. Their results indicate that approximately 83 percent of the atmospheric aldehydes in that area were due to motor vehicles. Furthermore, motor vehicles emit reactive hydrocarbons that can undergo photochemical oxidation to produce additional amounts of aldehydes (see discussion in Section 3.4.1).

3.4.2.1 Automobiles

The automobile is probably a major source of aldehyde air pollution. Estimations of aldehyde emission rates vary considerably, from 3.4 to 18.7 lb/1,000 gal of gasoline.[45,50,93,119,217] The reported emission data are summarized in Table 17 in the Appendix. From these data, it appears that the concentration of aldehydes emitted varies during the different engine modes in the following order: deceleration >> acceleration > cruise > idle. Other important factors in the amount of aldehydes emitted are type of gasoline and type of engine. The condition of the engine may also be a very important factor.[197]

Sigsby et al.[180] reported that aldehydes are present in diluted automobile exhaust to the extent of approximately 120 $\mu g/m^3$ (0.1 ppm) at atmospheric levels. Other studies on the irradiation of automobile exhaust indicate that approximately 10 to 20 percent of the atmospheric aldehydes may be due to the exhaust.[10,109]

Formaldehyde is the major aldehyde in automobile exhaust, accounting for 50 to 70 percent of the total aldehydes.[77,95,96] Acrolein accounts for approximately 3 to 10 percent (on mole basis) of the total aldehydes.[22,77]

Several other aldehydes have been identified in automobile exhaust; these include acetaldehyde,[31,68,77] propionaldehyde,[6,31,68] n-butyraldehyde,[68] iso-butyraldehyde,[6,68] trimethylacetaldehyde,[6] iso-valeraldehyde,[77] crotonaldehyde,[6,31,77] and benzaldehyde.[32,77]

3.4.2.2 Diesel Vehicles

Reported aldehyde emissions from diesel engines are given in Table 18 in the Appendix. The estimated emission rates are given as 10 to 16 lb/1,000 gal of fuel.[45,93] This is similar to that reported for automobiles (see Section 3.4.2.1). From these data it appears that the aldehyde emissions are usually lower at part loads and higher at no load or full load. Reckner _et al._[146] determined the amount of formaldehyde, acrolein, and aldehydes in emissions from diesel engines. These data indicate that formaldehyde generally constitutes 50 to 70 percent of the total aldehydes, and acrolein 5 to 10 percent of them.

3.4.2.3 Aircraft

Studies reporting aldehyde emissions from aircraft are summarized in Table 19 in the Appendix. The emission rate ranges from 0.2 to 2 pounds of aldehydes per hour for a four-engine jet aircraft; the total emissions per flight (including arrival and departure) range from 0.3 to over 4 pounds of aldehydes.[78,117,122,197] The principal aldehyde present in the jet-engine emissions was formaldehyde, generally accounting for greater than 60 percent of the total aldehydes.[117] It was estimated that 0.1 tons of aldehydes from aircraft were emitted per day in Los Angeles County in 1960. This figure was predicted to increase sixfold by 1965.[78]

3.4.3 Stationary Combustion Sources

Stationary combustion sources contribute to aldehyde air pollution. Although they are considered to be minor sources of aldehydes compared with automobile emissions and atmospheric photochemical reactions, these stationary combustion sources may contribute significantly if the equipment is not operating correctly or the control methods are inadequate.[197] Only the principal sources for which emission data were available are discussed in the following sections.

3.4.3.1 Combustion of Coal

Aldehydes and formaldehyde have been found in small amounts from sources that burn coal.[56,122,140,187] Wohlers and Bell[218] estimated the amount of aldehydes produced from the combustion of bituminous coal at 2 lb/ton of coal. Emission of aldehydes from anthracite coal was assumed to be 1 lb/ton of coal, based on the more complete combustion from higher flame temperatures. More recent data give the value at less than 0.01 lb/ton of coal.[122,140]

Formaldehyde emissions from different types of coal-burning power plants range from 0.06 to 0.25 ppm before the ash collector and 0.07 to 0.12 ppm after the ash collector.[56,187]

Data of emissions from combustion of coal are summarized in Table 20 in the Appendix.

3.4.3.2 Fuel Oil Combustion

Emission rates of aldehydes from sources using fuel oil range from nearly 0 to 14.8 lb/gal of oil, according to Hovey, Risman, and Cunnan.[93] The average for distillate oil (density of 7 lb/gal) was given as 2 pounds of aldehydes per 1,000 gallons of oil, while emission from residual oil (density of 8 lb/gal), which is used by the large consumers, was estimated at half that amount. Chass and George[44] summarized the results from various industrial and commercial oil-fired equipment. The data ranged from 3 to 52 ppm aldehydes in stack effluent or 0.02 to 1.8 pounds of aldehydes per hour. These results and others are summarized in Table 21 in the Appendix. The aldehyde emission rates vary with the type, size, and condition of the equipment. In fact, it is common to judge the operating condition of oil-fired equipment by the odor produced by aldehydes in the effluent gas.

3.4.3.3 Natural Gas Combustion

A summary of reported aldehyde emission data from the burning of natural gas in various home appliances and industrial equipment is shown in Table 22 in the Appendix. The aldehyde emissions vary from 2 to 49 ppm, depending on the source. Hovey, Risman, and Cunnan[93] reported a range of 0 to 60 pounds of aldehydes per million cubic feet of gas consumed, with an average of 10 $lb/10^6$ ft^3 of gas. They gave the average for propane and butane as 26 and 34 $lb/10^6$ ft^3

of gas, respectively. Weisburd,[214] on the other hand, reported aldehyde emissions from power plants as approximately 1 lb/10^6 ft^3 (0.02 lb/1,000 lb of gas) and for industrial use as 2 lb/10^6 ft^3 (0.1 lb/1,000 lb of gas). Vandaveer and Segeler[208] found formaldehyde and acetaldehyde in the emissions from burning natural, coke-oven, or butane gas. The aldehyde emissions may be much greater when no afterburners are used or when the correct air-to-fuel ratio is not maintained.

3.4.3.4 Incinerator Emissions

Table 23 in the Appendix summarizes the data on aldehyde emissions from different types of incinerators. Reported aldehyde emissions from multistage municipal incinerators average about 1.1 lb/ton of refuse (49 ppm).[93,122,197] However, emissions from small domestic incinerators vary from 0.1 to nearly 16 lb/ton of refuse (1 to 67 ppm).[93,197] Backyard incinerators have been reported to have emissions as high as 29 lb/ton (760 ppm).[197] Formaldehyde and acrolein are probably the principal aldehydes in the emissions.[98] Stenburg _et al._[189] reported that formaldehyde content in the emissions increases with (1) a decrease in gas temperature, (2) an increase in excess air, and (3) a decrease in refuse feed rate.

Alpiser[7] reported that aldehyde emission from a small-batch automobile incinerator (primary chamber holds one automobile) was 3 ppm with an afterburner or 16 ppm without an afterburner.

As a comparison, open-dump burning has been estimated at 3.0 to 4.0 pounds of aldehydes per ton of refuse,[93,122] or 6,000 pounds per day per million people.[64] Aldehyde emissions from open burning of paper and garden trimmings were estimated at 2.1 and 5.7 lb/ton of material, respectively.[93]

3.4.3.5 Emissions from Petroleum Refineries

Petroleum refineries are local sources of aldehyde emissions. A Los Angeles survey[29] indicated that catalytic cracking units emit 19 pounds of aldehydes per 1,000 barrels of feed (3 to 130 ppm) in the fluid unit and 12 lb/1,000 bl of feed in the thermofor units. Smaller amounts of aldehyde emissions also originate from the refineries' boilers, processor heaters, and compressor engines. Total aldehyde emissions from oil refineries for the Los Angeles area amount to approximately 2.4 tons/day. A summary of the emission factors is given in Table 24 in the Appendix.

3.4.4 Noncombustion Sources

When organic compounds are heated in the presence of air or an oxygen source, aldehydes and other oxygenated hydrocarbons may be produced. This is particularly true of the more reactive organic compounds such as olefins and aromatic compounds. Sources of this type of emission include industries manufacturing oxygenated organic compounds (e.g., aldehydes, alcohols, carboxylic acids) and processes in which solvents are removed by use of drying or baking ovens. Very little information is available on the aldehyde emissions from these sources. Some emission data from these sources can be found in Tables 25 and 26 in the Appendix.

3.4.4.1 Thermal Decomposition

In addition to the industrial sources of aldehydes via thermal decomposition of organic compounds mentioned above, the following examples illustrate other sources that may yield aldehydes in this manner. Babies placed in incubators following surgery were found to have respiratory problems caused by formaldehyde that had been formed by thermal decomposition of exhaled ether when it came in contact with the heating elements of the incubators.[129] Occupational and community exposure to acrolein may result from the thermal decomposition of glycerine from fats and oils.[141] Henson[87] suggested that acrolein is the important cause of the irritant effects from exposure to vapors from the cooking of fatty food over intense heat.

3.4.4.2 Drying or Baking Ovens

Processes in which organic solvents are heated may be local aldehyde emission sources which contribute to the overall aldehyde air pollution. A major process of this type is the coating of materials. The coating substance (dissolved in an organic solvent) is applied to the material, which is subsequently dried or baked in an oven to remove the solvent. Examples of operations using such procedures are automobile painting, coating of paper with resins or adhesives, and application of protective coatings to metals. Brunelle, Dickinson, and Hamming[41] determined the aldehyde, formaldehyde, and acrolein content of the effluent gases from several of these processes (see Table 26, Appendix). The solvents used included alkanes, aromatics, alcohols, and ketones. In each case, measurable amounts of aldehydes were produced with some values over 120,000 $\mu g/m^3$ (100 ppm) aldehydes (as formaldehyde). Maximum values for formaldehyde and acrolein were 62,400 $\mu g/m^3$ (52 ppm) and 25,000 $\mu g/m^3$ (10 ppm), respectively. The aldehyde concentration appeared to be higher in the samples taken after passing through the afterburner than in the samples taken at the oven before the afterburner. Similarly, data reported by Danielson[60] showed that the use of afterburners with paint-baking ovens may increase the aldehyde concentration up to tenfold, although almost complete removal of aldehydes is possible in some cases.

Wallach[212] analyzed the effluents from the baking of lithograph coatings in which mixtures of aliphatic and aromatic solvents were used. Total aldehydes ranged from 14,000 to 224,000 $\mu g/m^3$ (12 to 186 ppm) before passing through afterburners. Samples taken after the effluent passed through a high-temperature burner showed both an increase and a decrease in aldehyde concentration with no apparent pattern or reason. Samples taken after catalytic combustion treatment showed that aldehyde concentration increased up to 250 percent after treatment.

3.5 Environmental Air Concentrations

In 1967, the National Air Sampling Network began the monitoring of aldehydes.[126] The data for 1967, the latest available, are presented in Table 27 (Appendix). The averages ranged from 3 to 79 μg/m^3 of aldehyde (calculated as formaldehyde); the maximum values ranged from 5 to 161 μg/m^3.

Other areas reported aldehyde air concentrations before establishment of the National Air Sampling Network program. The data reported from 1951 to 1967 are given in Tables 28 and 29 in the Appendix. Until the early 1960's, the analysis method used was the sodium bisulfite method, which is not specific for aldehydes and is sensitive to some ketone as well (see discussion in Section 6.3.1).

Table 30 in the Appendix gives the aldehyde concentration in the air of different metropolitan areas (by population) in 1958 as reported by Wohlers and Bell[218] and cited by Stern.[194]

Cholak[49] reported that the aldehyde (calculated as formaldehyde) concentrations for the ambient air in several cities sampled in 1946 to 1951 ranged from 0 to 324 μg/m^3 (0 to 0.27 ppm), with the averages ranging from 48 to 216 μg/m^3 (0.04 to 0.18 ppm).

It is generally reported that of the aldehydes present in the atmosphere, 50 percent is accounted for as formaldehyde and 5 percent as acrolein.[17,109,147,167] Recent measurements have been made in El Monte and Huntington Park, Calif., for aliphatic aldehydes, formaldehyde, and acrolein.[174] The data, shown in Table 8, are for two high-oxidant days.

TABLE 8

CONCENTRATIONS OF ALDEHYDES IN ATMOSPHERE AT EL MONTE AND HUNTINGTON PARK, CALIF.[174]

($\mu g/m^3$)

Date 1968	Time P.S.T.	Aliphatic Aldehydes	Formaldehyde	Acrolein
EL MONTE, CALIF.				
10/22	0738	81.6	30.0	5.0
	0850	108.0	42.0	7.5
	0956	88.8	39.6	7.5
	1130	66.0	58.8	10.0
	1235	144.0	106.8	20.0
	1338	177.6	108.0	20.0
	1442	100.8		
10/23	0745			10.0
	0850	114.0	48.0	7.5
	1000	92.4	57.6	10.0
	1130	58.8	37.2	2.5
	1235	49.2	22.8	5.0
	1340	51.6	33.6	12.5
	1445			15.0
HUNTINGTON PARK, CALIF.				
10/22	0555	51.6	27.6	7.5
	0658	70.8	31.2	7.5
	0815	96.0	68.4	12.5
	0921	166.8	120.0	15.0
	1115	196.8	163.2	27.5
	1240	105.6	97.2	17.5
10/23	0545		32.4	10.0
	0647	46.8	28.8	7.5
	0904		91.2	20.0
	1010	207.6	116.4	25.0
	1208	146.4	109.2	20.0
	1330		60.0	15.0

4. ABATEMENT

Aldehydes are only some of the oxygenated hydrocarbons that are present in vehicle exhausts, incinerator effluents, and industrial emissions. Other compounds classified as oxygenated hydrocarbons are alcohols, ethers, ketones, carboxylic acids, and organic esters. Control methods for these oxygenated compounds, as well as for aldehydes, are considered under the hydrocarbon control programs. Control methods being currently studied include more effective combustion methods and the use of direct-flame and catalytic afterburners.

Although these methods generally decrease the amount of hydrocarbon emissions, they may actually produce greater amounts of aldehydes and other oxygenated hydrocarbons. Evidence for this can be seen from some of the data on aldehyde emissions from various sources given in Table 25 in the Appendix. In some cases, the amount of aldehydes increases tenfold by the use of afterburners in drying-oven processes.

5. ECONOMICS

No information has been found on the economic costs of aldehyde air pollution or on the costs of its abatement.

Data on the production and consumption of formaldehyde and acrolein are presented in Section 3.

6. METHODS OF ANALYSIS

There are numerous methods of analysis for aldehydes--too many to be covered thoroughly in this report. Only those methods that have been used for or appear applicable to determining formaldehyde, acrolein, or the "aliphatic" aldehydes in air samples or emission source samples will be discussed. Other methods of analysis for aldehydes can be found in the reviews of Altshuller,[9] Sawicki,[159] Altshuller et al.,[22] Farr,[69] and Reynolds and Irwin.[151]

6.1 Sampling Methods

Generally, common sampling methods employ bubblers or impingers containing a reactive reagent. In some cases the reactive reagent may result in a color product that may be used in the analysis procedure. Examples of the commonly used reagents are 3-methyl-2-benzothiazolone hydrazone (MBTH),[16,17,131,177] sodium bisulfite,[63,68,78] and a mixture of sodium bisulfite and sodium tetrachloromercurate-(II)[106,221] for "aldehydes"; chromotropic acid[17,22,114,177] for formaldehyde; and 4-hexylresorcinol[17,177] for acrolein. These reagents are preferred because they have high collection efficiencies (generally two bubblers in series yield 95 percent or better collection efficiencies) and produce fairly stable nonvolatile products, thus avoiding excess loss of aldehydes via evaporation or formation of undesirable by-products.

In some cases, water is used as the collection medium,[67,77,118] reportedly with high efficiency.

6.2 Qualitative Methods

The presence of aldehydes can be determined by infrared spectroscopy. The carbon-hydrogen stretch vibration of the aldehydic group adsorbs as a doublet in the 3.5 to 3.7 μ region. Furthermore, the carbonyl of an aldehydic group has an adsorption band in the 5.7 to 6.0 μ region, which, unlike the carbonyl bands of ketones and carboxylic acids, disappears when a chloroform solution is treated with phosphorus pentachloride.[161]

Many colorimetric methods applicable to formaldehyde, acrolein, and "aldehydes" have been used for spot tests or detector tube methods. Some of the more common methods are summarized in Table 9.

6.3 Quantitative Methods

6.3.1 Aldehydes

Recently one method has been used extensively to determine total water-soluble "aliphatic" aldehydes in atmospheric sampling.[17,34,35,90,91] Since 1967 this method has been used by the National Air Sampling Network of the National Air Pollution Control Administration[126] according to the procedure described by Morgan et al.[131] This method was first proposed by Sawicki et al.[167] and refined by Hauser and Cummins.[86,177] The latter method uses 3-methyl-2-benzothiazolone hydrazone (MBTH), with sulfuric acid added

TABLE 9

SUMMARY OF QUALITATIVE COLORIMETRIC DETERMINATION METHODS

Reagent	Color	Limits of Identification in Micrograms			
		Aldehydes	Formaldehyde	Acrolein	Ref.
Indole	Orange to red	~0.05-1	0.2		28
Fuchsin (Schiff method)	Violet to blue	~1-30	1		71
4-Phenylazo-phenyl-hydrazine sulfonic acid	Red to blue	0.2-0.4	0.25	0.2	71
2-Hydrazino-benzothiazole + p-nitrobenzenediazonium fluoborate	Blue to green	0.2-200	0.2	0.3	71, 163
2-Hydrazino-benzothiazole (HBT)	Blue	0.01-3.0	0.01		162
3-Methyl-2-benzothiazolone hydrazone (MBTH)	Blue	0.1-80	0.1		167
(J-acid) 6-amino-1-naphthol-3-sulfonic acid	Blue	0.01-11	0.03		164

to avoid the dilution necessary in the earlier procedures. The sensitivity is approximately 2.4 $\mu g/m^3$ (2 ppb), measured as formaldehyde. Aldehydes react with the MBTH to form a very stable product, which, upon oxidation with ferric chloride, produces a blue cationic dye that is measured at 628 mμ. Compounds which interfere with the analysis include aromatic amines, imino heterocyclics, carbazoles, azo dyes, stilbenes, Schiff bases, dinitrohydrazone (DNP) aldehyde derivatives, and compounds containing the p-hydroxy styryl group.[177] Since most of these compounds are not gaseous or water soluble, they will not generally interfere in analysis of atmospheric samples. Formaldehyde reacts in this procedure about 25 percent greater than the other aliphatic aldehydes and about 300 percent greater than branched-chained and unsaturated aldehydes. Altshuller and Leng[16] have suggested that a correction factor of 1.25 be used to take into account the various aldehyde responses to the method.

Most other colorimetric procedures that have been described in the literature show even larger response to formaldehyde in comparison with other aldehydes, and therefore, should not be used for quantitative determination of aldehydes.[9] Such methods include chromotropic acid, J-acid, phenyl J-acid, Schiff's reagent, and phenylhydrazine reagent (Schryver's method).

A continuous monitor method for "aldehydes,"[221] based on the method of Lyles et al.,[118] is a modified Schiff procedure using rosaniline and dichlorosulfulomercurate.

The sensitivity is reported as 12 μg/m^3 (0.01 ppm), with a collection efficiency of greater than 90 percent. Nitrogen dioxide can cause interference in concentrations of 0.5 ppm or more and its response to formaldehyde is greater than to other aldehydes.

Infrared spectroscopy has been used to determine aldehydes in irradiation chamber studies.[11,171] The carbon-hydrogen stretch vibration in the range of 3.5 to 3.7 μ was used.

The bisulfite method has been widely used for analysis of "aldehydes" in atmospheric samples,[147,149] automobile exhaust,[107] diesel exhaust,[36,173] and incinerator effluents.[220] However, this method measures both aldehydes and ketones and thus really measures carbonyls.[9] Furthermore, the sensitivity is not high, and the limit of applicability is approached with air sampling analysis. Therefore, this method is not very satisfactory for aldehyde analysis in air pollution.

Numerous methods have been reported for the separation and identification of specific aldehydes by use of derivatives such as 2,4-dinitrohydrazone (2,4-DNP).[9,159] Recently, gas chromatographic methods have been used for the separation and analysis of aldehydes that are collected as sodium bisulfite[68,112,113] or as 2,4-DNP derivatives.[77]

6.3.2 Formaldehyde

The colorimetric method of determining formaldehyde with chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid) has had widespread use. Several variations have been described in the literature.[21,22,40,147,215] The method proposed by Altshuller et al.[20,21] appears to be simple, rapid, and suitable for the analysis of effluents and air samples. The sensitivity of this method is approximately 12 $\mu g/m^3$ (0.01 ppm).[16] Nitrogen dioxide, most aldehydes and ketones, and straight-chain alcohols do not interfere significantly.[21,215] Aromatic hydrocarbons and olefins can cause serious interference, but the use of aqueous sodium bisulfite as the collection medium can reduce this interference. Furthermore, compounds that are easily converted via hydrolysis or oxidation to formaldehyde in strong, warm sulfuric acid may also interfere. Compounds of this type, which include sugars, formaldehyde polymers, glyoxal, piperonal, and related compounds, have been discussed by Sawicki.[159] The chromotropic acid method has been used in the analysis of air samples,[17,21] incinerator effluents,[189,190] automobile exhaust,[22] and diesel exhaust.[36,114,115,146]

Many other colorimetric methods have been used or appear applicable to analysis of air samples. Sawicki et al.[164,166] found that 6-amino-1-naphthol-3-sulfonic acid

(J-acid) and 6-anilino-1-naphthol-3-sulfonic acid (phenyl J-acid) have greater sensitivity than the chromotropic acid. However, these methods have not been used in analysis of effluents or air samples. A comparison of these methods and other spectrometric methods for determining formaldehyde has been made by Sawicki _et al_.[166] The results are shown in Table 31 in the Appendix.

A continuous method for determining formaldehyde with a sensitivity of 12 $\mu g/m^3$ (0.01 ppm) has been reported.[118,221] The method is a modified Schiff method using para-rosaniline in sodium tetrachloromercurate(II) and sodium bisulfite. This method has been used for analysis of air samples. Only two aldehydes, acetaldehyde and propionaldehyde, gave positive reactions.[118]

Polarographic methods[33,54] may also be applicable to analysis of air samples, but at present they need further study.

6.3.3 Acrolein

A highly sensitive spectrophotometric method for acrolein has been developed by Cohen and Altshuller,[51] who based their method on a reagent first proposed by Rosenthaler and Vegezzi.[153] Acrolein reacts with 4-hexylresorcinol in an ethanol-trichloroacetic acid solution to yield a blue-colored product with an absorption maximum at 605 $m\mu$. The sensitivity is approximately 12.5 $\mu g/m^3$ (0.005 ppm). The method appears selective; no significant interferences were found from sulfur dioxide, nitrogen dioxide, ozone, aromatic compounds, ketones, olefins, and other unsaturated aldehydes.[51,177] Slight interferences are found with some dienes[177] and with malonaldehyde, which appears to form a similar blue product. This method has been used in analysis of automobile exhaust,[22,51] diesel exhaust,[36,114,146] and atmospheric samples.[17,147]

Because colorimetric methods using tryptophan[141,178] and phloroglucinol[142,207] lack sufficient sensitivity and have appreciable interferences, they are not useful for analysis of air samples.[51] A J-acid method can be used to determine acrolein with a sensitivity of 0.01 μg, but serious interference results with equal or higher amounts of formaldehyde.[166]

Polarographic,[54] gas chromatographic,[68,94,134] and paper chromatographic methods have been used in the analysis of acrolein from vehicle exhaust and air samples. However, these methods have not been generally applied because of the complexity of the techniques.

7. SUMMARY AND CONCLUSIONS

The most characteristic and important effect of aldehydes--particularly of low molecular weight aldehydes--for both humans and animals is primary irritation of the eyes, upper respiratory tract, and skin. The observed symptoms in humans from inhalation of low concentrations of aldehydes include lacrimation, coughing, sneezing, headache, weakness, dyspnea, laryngitis, pharyngitis, bronchitis, and dermatitis. In most cases, the general and parenteral toxicities of these aldehydes appear to be related mainly to these irritant effects. The unsaturated aldehydes are several times more toxic than the corresponding aliphatic aldehydes. Also, the toxicity generally decreases with increasing molecular weight within the unsaturated and aliphatic aldehyde series. Sensitization has occurred from contact with formaldehyde solutions and other aldehydes, but sensitization of the pulmonary tract rarely is produced by inhalation of aldehydes. The anesthetic properties of aldehydes are generally overshadowed by the stronger irritant effects. Furthermore, concentrations that can be tolerated via inhalation can usually be metabolized so rapidly that systemic symptoms do not occur.

Formaldehyde concentrations as low as 600 $\mu g/m^3$ have been shown to cause cessation of the ciliary beat in rats. Animal experiments have shown that aldehydes can affect the responses of the respiratory system, causing such effects as an increase in flow resistance and in tidal volume and a decrease in the respiratory rate. Exposure of rats to 150 $\mu g/m^3$ of acrolein for 2 months caused a rise in the number of luminescent leukocytes in the blood. Exposure of animals to high concentrations of aldehydes has been shown by several investigators to produce edema and hemorrhages of the lungs and fluid in the pleural and peritoneal cavities. In a Russian study, formaldehyde was found to prolong the mean duration of pregnancy in rats and decrease the number of offspring. In addition, the weight of the lungs and liver of the offspring was less than that of the controls' offspring, but other organs exhibited an increase in weight.

Animal experiments also indicate possible synergistic effects between aldehydes and aerosols. Thus, acrolein and formaldehyde in the presence of certain inert aerosols appeared to be more toxic to mice than the pure compounds. Experiments with guinea pigs showed that formaldehyde with sodium chloride aerosols produced significant increases in the "respiratory work" compared with the effect of the pure vapor.

In addition to the toxic effects, aldehydes may contribute to the annoyances of odor and eye irritation caused by polluted air. Aldehyde concentrations have been shown to correlate with the intensity of odor of diesel exhaust and the intensity of eye irritation during natural and chemically produced smogs. Data indicate that as little as 12 $\mu g/m^3$ of formaldehyde can cause human eye response.

Aldehyde air pollution may result in oxidant-type damage to plants, although atmospheric photochemically produced products from the aldehydes may actually cause the damage rather than direct attack by aldehydes.

There are no data available to indicate the effect of aldehyde air pollution on materials.

Vehicle exhaust, particularly from automobiles, appears to be the major emission source of aldehydes. However, significant amounts may also be produced from other combustion sources such as open burning and incineration of solid waste materials, and the burning of fuels (gas, fuel oil, coal). Another source of aldehyde emission is the thermal decomposition of hydrocarbons by pyrolysis in the presence of air or oxygen. Sources of these emissions include chemical manufacturing plants and industries that use drying or baking ovens to remove organic solvents in such processes as automobile painting and the manufacture of coated paper and metals.

Air sampling data indicate that plants manufacturing formaldehyde may be local sources of aldehyde pollution; over 4 billion pounds of formaldehyde were manufactured in the United States in 1968. However, the major amount of aldehyde pollution in some areas of the United States is from the photochemical reaction between nitrogen oxides and hydrocarbons. Hydrocarbons that yield formaldehyde are olefins, and to a lesser degree, other aldehydes and aromatic hydrocarbons. Diolefins produce most of the atmospheric acrolein. Some data indicate that in certain areas over two-thirds of the atmospheric aldehydes may have resulted from photochemical reactions. Of course, the sources that emit aldehyde pollutants are generally the same as those emitting hydrocarbons and nitrogen oxides.

In addition, aldehydes themselves may undergo photochemical reactions. They may produce, at low partial pressures in the presence of nitrogen oxides, other products such as carbon monoxide, lower aldehydes, nitrates, and oxidants. The oxidants produced include ozone, peroxyacyl nitrates, and alkyl hydroperoxides (hydrogen peroxide in the case of formaldehyde). No peroxyacids or diacetyl peroxides are found at low partial pressures of aldehydes.

In 1967 the National Air Sampling Network began to report data for aliphatic aldehydes. The data for 1967 for several cities show that the average concentrations of aldehydes ranged from 3 to 79 $\mu g/m^3$ and that the maximum values ranged from 5 to 161 $\mu g/m^3$. A Los Angeles area report indicates that the maximum values for two "smog" days in 1968 were 208 $\mu g/m^3$ for aliphatic aldehydes, 163 $\mu g/m^3$ for formaldehyde, and 27 $\mu g/m^3$ for acrolein. Generally, formaldehyde accounts for 50 percent or more of the total aldehydes, while acrolein accounts for about 5 percent.

Control of aldehyde emissions is being studied along with current hydrocarbon (organic) control programs. However, the use of certain combustion control techniques such as catalytic afterburners, may cause an increase in the amount of aldehydes emitted.

No information has been found on the economic costs of aldehyde air pollution or on the costs of its abatement.

Colorimetric determination methods, satisfactory for analysis of air samples, have been reported for aliphatic aldehydes (sensitivity approximately 2.4 $\mu g/m^3$ or 2 ppb), formaldehyde (sensitivity approximately 12 $\mu g/m^3$ or 10 ppb), and acrolein (sensitivity approximately 12.5 $\mu g/m^3$ or 5 ppb). A continuous method for determining "aldehydes" based on a modified Schiff method with a sensitivity of 12 $\mu g/m^3$ (0.01 ppm) has been reported.

Based on the material presented in this report, further studies are suggested in the following areas:

(1) Identification of all the aldehydes present in the atmosphere and their approximate concentration ranges. Determination of the concentration, geographical distribution, and time distribution of the aldehydes that appear to have important effects.

(2) Expansion of research concerning the effects on humans, animals, and plants of long-term exposure to low concentrations of each of the aldehydes present in the atmosphere, particularly formaldehyde and the unsaturated aldehydes.

(3) Expansion of research on the hydrocarbon control methods for simultaneous reduction of aldehyde emissions.

(4) Determination of the contribution of atmospheric photochemical reactions in aldehyde air pollution, particularly in metropolitan areas.

REFERENCES

1. Air Pollution/Chemung County (Supplement to Comprehensive Area Survey Report Number One (Greater Elmira), New York State Air Pollution Control Board, Albany (1965).

2. Air Pollution in Erie County (Comprehensive Area Survey Report Number Two), New York State Air Pollution Control Board, Albany (1963).

3. Air Pollution/The Mid-Hudson: Greene, Ulster, Rockland, Columbia, Dutchess (Comprehensive Area Survey Report Number Six), New York State Air Pollution Control Board, Albany (Feb. 1966).

4. Air Pollution in Westchester, New York State Air Pollution Control Board, Albany (Dec. 1965).

5. Alkire, G. J. and C. R. Wyss, Air Quality Survey at Selected Sites on the Hanford Project, Pacific Northwest Lab., Richland, Wash., Dept. of Environmental and Radiological Sciences (Nov. 1967).

6. Alperstein, M., and R. L. Bradow, Exhaust Emissions Related to Engine Combustion Reactions, Society of Automotive Engineers, Fuels and Lubricants Meeting, Houston, Tex. (Nov. 1-3, 1966).

7. Alpiser, F. M., Air Pollution from Disposal of Junk Autos, Presented at the 61st Annual Meeting of the Air Pollution Control Association, St. Paul, Minn. (June 23-27, 1968).

8. Altshuller, A. P., Reactivity of Organic Substances in Atmospheric Photooxidation Reactions, Intern. J. Air Water Pollution (Great Britain) 10:713 (1966).

9. Altshuller, A. P., "Analysis of Aliphatic Oxygenated Compounds," in Air Pollution, vol. 2, A. C. Stern, Ed. (New York: Academic Press, p. 130, 1968).

10. Altshuller, A. P., Director; Division of Chemistry and Physics, National Air Pollution Control Administration, Cincinnati, Ohio, personal communication (May, 1969).

11. Altshuller, A. P., and J. J. Bufalini, Photochemical Aspects of Air Pollution: A Review, Photochem. Photobiol. 4:97 (1965).

12. Altshuller, A. P., and I. R. Cohen, Atmospheric Photooxidation of the Ethylene-Nitric Oxide System, Accepted for publication by J. Air and Water Pollution, Presented at Symposium on Air Pollution, 145th Meeting American Chemical Society, New York (Sept. 8-13, 1963).

13. Altshuller, A. P., and I. R. Cohen, Structural Effects on the Rate of Nitrogen Dioxide Formation in the Photo-Oxidation of Organic Compound-Nitric Oxide Mixtures in Air, Intern. J. Air Water Pollution 7:787-97 (1963).

14. Altshuller, A. P., and I. R. Cohen, Photo-oxidation of Acrolein-Nitrogen Oxide Mixtures in Air, Intern. J. Air Water Pollution 7:1043 (1963).

15. Altshuller, A. P., and I. R. Cohen, Atmospheric Reactions of Propionaldehyde in Air Mixtures, Atmospheric Environ. 1(3):319 (1967).

16. Altshuller, A. P., and L. J. Leng, Application of the 3-Methyl-2-Benzothiazolone Hydrazone Method for Atmospheric Analysis of Aliphatic Aldehydes, Anal. Chem. 35(10):1541 (1963).

17. Altshuller, A. P., and S. P. McPherson, Spectrophotometric Analysis of Aldehydes in the Los Angeles Atmosphere, J. Air Pollution Control Assoc. 13(3):109 (1963).

18. Altshuller, A. P., I. R. Cohen, and T. C. Purcell, Photooxidation of Propionaldehyde at Low Partial Pressure of Aldehyde, Can. J. Chem. 44:2973 (1966).

19. Altshuller, A. P., I. R. Cohen, and T. C. Purcell, Photooxidation of Hydrocarbons in the Presence of Aliphatic Aldehydes, Science 156(3777):937 (1967).

20. Altshuller, A. P., L. J. Leng, and A. F. Wartburg, Jr., Source and Atmospheric Analyses for Formaldehyde by Chromotropic Acid Procedures, Intern. J. Air Water Pollution 6:381 (1962).

21. Altshuller, A. P., D. L. Miller, and S. F. Sleva, Determination of Formaldehyde in Gas Mixtures by the Chromotropic Acid Method, Anal. Chem. 33(4):622 (1961).

22. Altshuller, A. P., et al., Analysis of Aliphatic Aldehydes in Source Effluents and in the Atmosphere, Anal. Chim. Acta 25:101 (1961).

23. Altshuller, A. P., _et al._, Products and Biological Effects from Irradiation of Nitrogen Oxides with Hydrocarbons or Aldehydes Under Dynamic Conditions, _Intern. J. Air Water Pollution_ _10_:81 (1966).

24. Amdur, M. O., The Physiological Response of Guinea Pigs to Atmospheric Pollutants, _Intern.J. Air Water Pollution_ _1_:170 (1959).

25. Amdur, M. O., The Effect of Aerosols on the Response to Irritant Gases, Inhaled Particles Vapours, Proc. Intern. Symp., Oxford, Eng. ,pp. 281-92 (1960).

26. Amdur, M. O., The Response of Guinea Pigs to Inhalation of Formaldehyde and Formic Acid Alone and With a Sodium Chloride Aerosol, _Intern. J. Air Water Pollution_ _3_(4):201 (1960).

27. Anderson, D. M., J. Lieben, and V. H. Sussman, Pure Air For Pa., Pennsylvania Dept. of Health and Public Health Service, U. S. Dept of Health, Education,and Welfare (1961).

28. Anger, V., and G. Fischer, A New Spot Reaction of Aldehydes, _Mikrochim. Acta_, p. 592 (1960).

29. Atmospheric Emissions from Petroleum Refineries (A Guide for Measurement and Control), Public Health Service, Cincinnati, Ohio, Division of Air Pollution (1960).

30. Atmospheric Pollution in the Great Kanawha River Valley Industrial Area, Bureau of Industrial Hygiene, West Virginia State Dept. of Health, Charleston, Bureau of Industrial Hygiene, and Cincinnati Univ., Ohio, Kettering Lab. (1952).

31. Barber, E. D., and J. P. Lodge, Jr., Paper Chromatographic Identification of Carbonyl Compounds as Their 2,4-Dinitrophenylhydrazones in Automobile Exhaust, _Anal. Chem._ _35_:348 (1963).

32. Barber, E. D., and E. Sawicki, The Separation and Identification of Aromatic Carbonyl Compounds as Their 4- itrophenylhydrazones in Automobile Exhaust by Paper and Thin-Layer Chromatography, Dept. of Health, Education, and Welfare, Public Health Service, Cincinnati, Ohio (1967).

33. Barnes, E. C., and H. W. Speicher, The Determination of Formaldehyde in Air, J. Ind. Hyg. Toxicol 24:9 (1942).

34. Basbagill, W. J., Air Contaminant Measurements at Roosevelt Field, Nassau County, New York (January-February 1964), Public Health Service, Cincinnati, Ohio, Division of Air Pollution (July 1965).

35. Basbagill, W. J., and J. L. Dallas, Air Quality in Boston, Massachusetts (November-December 1963), Public Health Service, Cincinnati, Ohio, Division of Air Pollution (Nov. 1964).

36. Battigelli, M. C., Air Pollution from Diesel Exhaust, J. Occupational Med. 5:54 (1963).

37. Berger, L. B., and R. T. Artz, Rept. Invest. 4287 U. S. Bur. of Mines (May 1948).

38. Bourne, H. G., Jr., and S. Seffrin, Formaldehyde in Wrinkleproof Apparel Produces Tears for Milady, Ind. Med. Surg. 28:232 (1959).

39. Brennan, E. G., I. A. Leone, and R. H. Daines, Atmospheric Aldehydes Related to Petunia Leaf Damage, Science 143(3608):818 (1964).

40. Bricker, C. E., and A. H. Vail, Microdetermination of Formaldehyde With Chromotropic Acid, Anal. Chem. 22:720 (1950).

41. Brunelle, M. F., J. E. Dickinson, and W. J. Hamming, Effectiveness of Organic Solvents in Photochemical Smog Formation (Solvent Project, Final Rept.), Air Pollution Control District, Los Angeles County, Calif., Evaluation and Planning Division (July 1966).

42. Calvert, J. G., and P. L. Hanst, The Mechanism of the Photooxidation of Acetaldehyde At Room Temperature, Can. J. Chem. 37:1671 (1959).

43. Catilina, P., L. Thieblot, and J. Champeix, Experimental Lesions of the Respiratory System of Rats from Inhalation of Acrolein, Arch. des Maladies Professionelles 27:857 (1966).

44. Chass, R. L., and R. E. George, Contaminant Emission from Combustion of Fuels, J. Air Pollution Control Assoc. 10:34 (1960).

45. Chass, R. L., et al., Total Air Pollution Emissions in Los Angeles County, J. Air Pollution Control Assoc. 10:351 (1960).

46. Chemical Reactions in Los Angeles Smog, *Proc. Natl. Air Pollution Symp., 2nd*, Pasadena, Calif., pp. 28-34 (1952).

47. Chemical Safety Data Sheet SD-1, Properties and Essential Information for Safe Handling and Use of Formaldehyde, Rev. April 1960, Mfg. Chemists' Assn., Washington, D.C.

48. Chemical Safety Data Sheet SD-85, Properties and Essential Information for Safe Handling and Use of Acrolein, Adopted 1961, Mfg. Chemists' Assn., Washington, D.C.

49. Cholak, J., *Proc. Natl. Air Pollution Symp., 2nd.*, Pasadena, Calif., pp. 6-15 (May 5-6, 1952).

50. Clean Air for California, State of California, Dept. of Public Health (March 1955).

51. Cohen, I. R., and A. P. Altshuller, A New Spectrophotometric Method for the Determination of Acrolein in Combustion Gases and in the Atmosphere, *Anal. Chem.* *33*(6):726 (1961).

52. Community Air Quality Guides--Aldehydes, *Am. Ind. Hyg. Assoc. J.* *29*(5):505 (1968).

53. Conlee, C. J., *et al*., Motor Vehicle Exhaust Studies at Three Selected Sites, Preprint (1964).

54. Coulson, D. M., Polarographic Determination of Semicarbazones, *Anal. Chim. Acta* *19*:284 (1958).

55. Cralley, L. V., The Effect of Irritant Gases Upon Rate of Ciliary Activity, *J. Ind. Hyg. & Toxicol.* *24*:193 (1942).

56. Cuffe, S. T., and R. W. Gerstle, Emissions from Coal-Fired Power Plants: A Comprehensive Summary, National Center for Air Pollution Control, *U.S. Public Health Serv. Publ. 999-AP-35* (1967).

57. Cvetanovic, R. J., Electrophilic Character of Oxygen Atoms, *Can. J. Chem.* *38*:1678 (1960).

58. Dahle, E. W., Jr., Annual Report of the Bureau of Industrial Hygiene, 1966, Baltimore City Health Dept., Md., Bureau of Industrial Hygiene (1966).

59. Dalhamn, T., and J. Rhodin, Mucous Flow and Ciliary Activity in Trachea of Healthy Rats and Rats Exposed to Irritant Gases, Acta Physiol. Scandinav. 36 (Suppl. 123):1-16 (1956).

60. Danielson, J. A., Air Pollution Engineering Manual, U.S. Dept. of Health, Education, and Welfare, Public Health Service, Cincinnati, Ohio (1967).

61. Darley, E. R., J. T. Middleton, and M. J. Garber, Plant Damage and Eye Irritation from Ozone-Hydrocarbon Reactions, Agr. Food Chem. 8(6):483 (1960).

62. Davis, T. R. A., S. P. Battista, and C. J. Kensler, Mechanism of Respiratory Effects During Exposure of Guinea Pigs to Irritants, Arch. Environ. Health 15(4): 412 (1967).

63. Devorkin, H., et al., Air Pollution Source Testing Manual, Air Pollution Control District, Los Angeles County, Calif. (1965).

64. Eliassen, R., Domestic and Municipal Sources of Air Pollution, Proc. National Conference on Air Pollution (Nov. 18-20, 1958); U. S. Public Health Serv. Publ. 654, Washington, D. C. (1959).

65. Elliott, M. A., and R. F. Davis, Composition of Diesel Exhaust Gas, Presented at S.A.E. National Diesel Engine Meeting, St. Louis (Nov. 1949).

66. Elliott, M. A., G. J. Nebel, and F. G. Rounds, The Composition of Exhaust Gases from Diesel, Gasoline and Propane Powered Motor Coaches, J. Air Pollution Control Assoc. 5(2):103 (1955).

67. Ellis, C. F., Chemical Analyses of Automobile Exhaust Gases for Oxygenates, Bur. Mines Rept. Invest. 5822 (1961).

68. Ellis, C. F., R. F. Kendall, and B. H. Eccleston, Identification of Some Oxygenates in Automobile Exhausts by Combined Gas Liquid Chromatography and Infrared Techniques, Anal. Chem. 37(4):511 (1965).

69. Farr, J. P. G., Analyses for the Industry, Ind. Chemist 389 (1956).

70. Fassett, D. W., "Aldehydes and Acetals," in Industrial Hygiene and Toxicology, vol. II, F. A. Patty, Ed. (New York: Interscience, 1963).

71. Feigl, F., Spot Tests in Organic Analysis (New York: Elsevier, 1956).

72. Fiero, G. W., Solvents, Smog and Rule 66, J. Am. Soc. Lubrication Engrs. 23(11):448 (1967).

73. Fleckenstein, L. J., Aldehydes, in Kirk-Othmer Encyclopedia of Chemical Technology, vol. 1 (New York: Interscience, p. 639, 1963).

74. Formaldehyde--Controlling Chemical Hazards, Ser. No. 3, U. S. Dept. of Labor, Govt. Printing Office, Washington, D. C. (1945).

75. Formaldehyde Finds New Pastures, Chemical Week 95(23):113 (1964).

76. Formaldehyde, Its Toxicity and Potential Dangers, Supplement, Public Health Rept. U.S. 181 (1945).

77. Fracchia, M. F., F. J. Schuette, and P. K. Mueller, A Method for Sampling and Determination of Organic Carbonyl Compounds in Automobile Exhaust, Environ. Sci. Technol. 1(11):915 (1967).

78. George, R. E., and R. M. Burlin, Air Pollution from Commercial Jet Aircraft in Los Angeles County, Los Angeles County Air Pollution Control District, Calif. (Apr. 1960).

79. Gofmekler, V. A., Effect of Embryonic Development of Benzene and Formaldehyde in Inhalation Experiments, Hyg. Sanitation 33:327 (1968).

80. Guest, H. R., B. W. Kiff, and H. A. Stansbury, Acrolein and Derivatives, in Kirk-Othmer Encyclopedia of Chemical Technology, vol. 1 (New York: Interscience, pp. 255-274, 1963).

81. Gusev, M. I., et al., Determination of the Daily Average Maximum Permissible Concentration of Acrolein in the Atmosphere, Hyg. and Sanitation 31(1):8 (1966).

82. Haagen-Smit, A. J., et al., Investigation on Injury to Plants from Air Pollution in the Los Angeles Area, Plant Physiol. 27:18 (1952).

83. Haggard, H. W., Action of Irritant Gases Upon Respiratory Tract, J. Ind. Hyg. 5:390 (1923).

84. Hamming, W. J., and R. D. MacPhee, Relationship of Nitrogen Oxides in Auto Exhaust to Eye Irritation--Further Results of Chamber Studies, Atmospheric Environ. 1(5):577 (1967).

85. Hangebrauck, R. P., D. S. von Lehmden, and J. E. Meeker, Emissions of Polynuclear Hydrocarbons and Other Pollutants from Heat-Generation and Incineration Processes, Public Health Service, U. S. Dept. of Health, Education, and Welfare, for Presentation at the Air Pollution Control Assoc. Annual Meeting, Paper No. 63-49 (June 1963).

86. Hauser, T. R., and R. L. Cummins, Increasing Sensitivity of 3-Methyl-2-Benzothiazolone Hydrazone Test for Analysis of Aliphatic Aldehydes in Air, Anal. Chem. 36(3):679 (1964).

87. Henson V. E., Toxicology of Some of the Aliphatic Aldehydes, J. Occupational Med. 1:457 (1959).

88. Hindawi, I. J., and A. P. Altshuller, Plant Damage Caused by Irradiation of Aldehydes, Science 146(3643):540 (1964).

89. Hitchcock, L. B., et al., Air Pollution Situation in Los Angeles -- An Aerometric Survey, Proc. Natl. Air Pollution Symp., 3rd, Pasadena, Calif., pp. 12-23 (1955).

90. Hochheiser, S., M. Burchett, and H. J. Dunsmore, Air Pollution Measurements in Pittsburgh (January-February 1963), Public Health Service, Cincinnati, Ohio, Division of Air Pollution and Alleghany County Health Dept., Pittsburgh, Pa., Bureau of Air Pollution Control (Nov. 1963).

91. Hochheiser, S., M. Nolan, and H. J. Dunsmore, Air Pollution Measurements in Duquesne, Pennsylvania (September-October 1963), Public Health Service, Cincinnati, Ohio, Division of Air Pollution and Allegheny County Health Dept., Duquesne, Pa., Bureau of Air Pollution Control (Oct. 1964).

92. Hornedo, M. D., and J. H. Tillman, Air Pollution in the El Paso, Texas Area, El Paso City, County Health Unit, Tex. (1959).

93. Hovey, H. H., A. Risman, and J. F. Cunnan, The Development of Air Contaminant Emission Tables for Nonprocess Emissions, Presented at the 58th Annual Meeting, Air Pollution Control Assoc., Toronto, Canada, Paper No. 65-17 (June 20-24, 1965).

94. Hughes, K. J., and R. W. Hurn, A Preliminary Study of Hydrocarbon-Derived Oxygenated Material in Automobile Exhaust Gases, J. Air Pollution Control Assoc. 10:367 (1960).

95. Hurn, R. W., Comprehensive Analyses of Automotive Exhausts, Arch. Environ. Health 5:592 (1962).

96. Hurn, R. W., et al., The Potpourri That is Exhaust Gas, Am. Petrol. Inst., Proc. 42(3):657 (1962).

97. Interstate Air Pollution Study, Phase II Report, Section II, Air Pollutant Emission Inventory, U. S. Dept. of Health, Education, and Welfare, Public Health Service (1966).

98. Jacobs, M. B., Health Aspects of Air Pollution from Incinerators, Proc. Natl. Incinerator Conf., New York, pp. 128-31 (1964).

99. Kaiser, E. R., et al., Performance of a Flue-Fed Incinerator, J. Air Pollution Control Assoc. 9(2):85 (1959).

100. Katz, M., Some Aspects of the Physical and Chemical Nature of Air Pollution, World Health Organ. Monograph Ser. 46, pp. 97-158 (1961).

101. Kensler, C. J., and S. P. Battista, Chemical and Physical Factors Affecting Mammalian Ciliary Activity, Am. Rev. Respirat. Diseases 93(3):93 (1966).

102. Kinosian, J. R., J. A. Maga, and J. R. Goldsmith, The Diesel Vehicle and Its Role in Air Pollution, State of California, Dept. of Public Health, Bureau of Air Sanitation, Berkeley, Calif. (1962).

103. Kopczynski, S. L., Photo-Oxidation of Alkylbenzene-Nitrogen Dioxide Mixtures in Air, Intern.J. Air Water Pollution 8:107 (1964).

104. Kreichelt, T. E., and E. W. Dahle, Jr., Air Pollution Measurements in Baltimore, Md. (March and April 1964), Public Health Service, Cincinnati, Ohio, Division of Air Pollution and Bureau of Industrial Hygiene, Md., Baltimore City Health Dept. (Nov. 1964).

105. LaBelle, C. W., J. E. Long, and E. E. Christofano, Synergistic Effects of Aerosols, A.M.A. Arch. Ind. Health 11:297 (1955).

106. Lahmann, E., and K. Jander, Determination of Formaldehyde from Street Air, Text in German. Gesundh. Ingr. (Munich) 89(1):18 (1968).

107. Larson, G. P., J. C. Chipman, and E. K. Kauper, Study of the Distribution and Effects of Auto Exhaust Gas, J. Air Pollution Control Assoc. 5:84 (1955).

108. Larson, G. P., G. I. Fischer, and W. J. Hamming, Evaluating Sources of Air Pollution, Ind. Eng. Chem. 45:1070 (1953).

109. Leach, P. W., *et al*., Effects of HC/NO_x Ratios of Irradiated Auto Exhaust, Part II, J. Air Pollution Control Assoc. 14:176 (1964).

110. Leighton, P. A.,"Photochemical Aspects of Air Pollution," in Physical Chemistry, vol. IX (New York: Academic Press, 1961).

111. Leonardos, G., D. A. Kendall, and N. J. Barnard, Odor Threshold Determinations of 53 Odorant Chemicals, J. Air Pollution Control Assoc. 19:91 (1969).

112. Levaggi, D. A., and M. Feldstein, Gas Chromatographic Determination of Aldehydes, Bay Area Air Pollution Control District, San Francisco, Calif. Presented at State Health Dept. Methods Conference, Pasadena, Calif. (Feb. 7-9, 1968).

113. Levaggi, D. A., and M. Feldstein, The Collection and Analysis of Low Molecular Weight Carbonyl Compounds from Source Effluents, J. Air Pollution Control Assoc. 19:43 (1969).

114. Linnell, R. H., and W. E. Scott, Diesel Exhaust Analysis (Preliminary Results), Arch. Environ. Health 5:616 (1962).

115. Linnell, R. H., and W. E. Scott, Diesel Exhaust Composition and Odor Studies, J. Air Pollution Control Assoc. 12:510 (1962).

116. Louw, C. W., Atmospheric Pollutants and Their Analysis, C.S.I.R. Special Report Smog 2, South African Council for Scientific and Industrial Research, Pretoria (1966).

117. Lozano, E. R., W. W. Melvin, and S. Hochheiser, Air Pollution Emissions from Jet Engines, Presented at 60th Annual Meeting Air Pollution Control Assoc., Cleveland, Ohio (June 11-16, 1967).

118. Lyles, G. R., F. B. Dowling, and V. J. Blanchard, Quantitative Determination of Formaldehyde in the Parts Per Hundred Million Concentration Level, J. Air Pollution Control Assoc. 15(3):106 (1965).

119. Magill, P. L., and R. W. Benoliel, Air Pollution in Los Angeles County: Contribution of Industrial Products, Ind. Eng. Chem. 44:1347 (1952).

120. Magill, P. L., F. R. Holden, and C. Ackley, Air Pollution Handbook (New York: McGraw-Hill, 1956).

121. Mathews, D. S., and J. J. Schueneman, Management of Dade County's Air Resources, U. S. Dept. of Health, Education and Welfare, Public Health Service, Cincinnati, Ohio (1962).

122. Mayer, M., A Compilation of Air Pollutant Emission Factors for Combustion Processes, Gasoline Evaporation, and Selected Industrial Processes, Public Health Service, Cincinnati, Ohio (1965).

123. McDowell, C. A., and L. K. Sharples, The Photochemical Oxidation of Aldehydes in the Gaseous Phase, Part 1, Can. J. Chem. 36:251 (1958).

124. McDowell, C. A., and L. K. Sharples, The Photochemical Oxidation of Aldehydes in the Gaseous Phase, Part 2, Can. J. Chem. 36:258 (1958).

125. McDowell, C. A., and S. Sifniades, Oxygen-18 Tracer Evidence for the Termination Mechanism in the Photochemical Oxidation of Acetaldehyde, Can. J. Chem. 41:300 (1963).

126. McMullen, T. B., Technical Reports Unit, Division of Air Quality and Emission Data, National Air Pollution Control Administration, personal communication (May, 1969).

127. Melekhina, V. P., Maximum Permissible Concentration of Formaldehyde in Atmospheric Air, USSR Literature on Air Pollution and Related Occupational Diseases 3:135 (1960).

128. Melekhina, V. P., Hygienic Evaluation of Formaldehyde as an Atmospheric Air Pollutant, U.S.S.R. Literature on Air Pollution and Related Occupational Diseases 9:9 (1962).

129. Mendenhall, M. K., J. A. Jenicek, and J. M. Bryant, Thermal Decomposition of Ether in the Infant Incubator, *J. Am. Med. Assoc.* *173*:651 (1960).

130. *The Merck Index*, 8th ed. (Rahway, N. J.: Merck, 1968).

131. Morgan, G. B., C. Golden, and E. C. Tabor, New and Improved Procedures for Gas Sampling and Analysis in the National Air Sampling Network, *J. Air Pollution Control Assoc.* *17*:300 (1967).

132. Morrill, E. E., Jr., Formaldehyde Exposure from Paper Process Solved by Air Sampling and Current Studies, *Air Cond. Heat. Ventilating* *58*:94 (1961).

133. Motor Vehicles, Air Pollution and Health. A Report of the Surgeon General to the U. S. Congress, 87th Congress, 2nd Session, House Document No. 489, Dept. of Health, Education, and Welfare, Public Health Service, Washington, D. C. (June 1962).

134. Mueller, P. K., M. F. Fracchia, and F. J. Schuette, 152nd National Meeting, Am. Chem. Soc., New York (1966).

135. Murphy, S. D., and C. E. Ulrich, Multi-Animal Test System for Measuring Effects of Irritant Gases and Vapors on Respiratory Function of Guinea Pigs, *Am. Ind. Hyg. Assoc. J.* *25*:28 (1964).

136. Murphy, S. D., H. V. Davis, and V. L. Zaratzian, Biochemical Effects in Rats from Irritating Air Contaminants, *Toxicol. Appl. Pharmacol.* *6*(5):520 (1964).

137. Murphy, S. D., D. A. Klingshirn, and C. E. Ulrich, Respiratory Response of Guinea Pigs During Acrolein Inhalation and Its Modification by Drugs, *J. Pharm. Exptl. Therap. 141* (1963).

138. Orning, A. A., C. H. Schwartz, and J. F. Smith, A Study of the Minor Products of Coal Combustion, Am. Soc. Mech. Engrs., Paper 64-PWR-4, Presented at the IEEE-ASME National Power Conference, Tulsa, Okla. (Sept. 27-Oct. 1, 1964).

139. Paul, F. M., Report to the Committee on Air Pollution, Memo 31, Fuel Research Station, London (1954).

140. Perry, H., and J. H. Field, Air Pollution and the Coal Industry, *Trans. AIME* *238*(4):337 (1967).

141. Plotnikova, M. M., Acrolein As an Atmospheric Air Pollutant, Gigiena i Sanit. 22:10 (1957); Translated by B. S. Levine, U.S.S.R. Literature on Air Pollution and Related Occupational Diseases 3:188 (May 1960).

142. Powick, W. C., A New Test for Acrolein and Its Bearing on Rancidity in Fats, Ind. Eng. Chem. 15:66 (1923).

143. Prentiss, A. M., Chemicals in War (New York: McGraw-Hill, 1937).

144. Purcell, T. C., and I. R. Cohen, Microdetermination of Peroxides by Kinetic Colorimetry, Environ. Sci. Technol. 1:431 (1967).

145. Purcell, T. C., amd I. R. Cohen, Photooxidation of Formaldehyde at Low Partial Pressures of Aldehyde, Environ. Sci. Technol. 1:845 (1967).

146. Reckner, L. R., W. E. Scott, and W. F. Biller, The Composition and Odor of Diesel Exhaust, Proc. Am. Petrol. Inst. 45:133 (1965).

147. Renzetti, N. A., and R. J. Bryan, Atmospheric Sampling for Aldehydes and Eye Irritation in Los Angeles Smog--1960, J. Air Pollution Control Assoc. 11(9):421 (1961).

148. Renzetti, N. A., and E. A. Schuck, Preliminary Observations on the Relationship Between Eye Irritation in Synthetic Systems and in the Atmosphere, Stanford Research Inst., South Pasadena, Southern California Labs (1960).

149. Renzetti, N. A., L. H. Rogers, and R. Tice, in An Aerometric Survey in the Los Angeles Basin, August-November 1954, N. A. Renzetti, ed., Report No. 9, Air Pollution Foundation, Los Angeles, Calif. (1955).

150. A Review of Air Pollution in New York State, New York State Air Pollution Control Board, Albany (July 1958).

151. Reynolds, J. G., and M. Irwin, The Determination of Formaldehyde and Other Aldehydes, Chem. Ind. 419 (1948).

152. Robison, C. B., J. C. Chambers, and J. W. Bates, Defining the Problem of Air Pollution in Metropolitan Birmingham, Alabama, Preprint, Ala. Jefferson County Dept. of Health (1967).

153. Rosenthaler, L., and G. Vegezzi, Detection and Determination of Acrolein in Alcoholic Liquors, Lebensm-Untersuch U. Forsch.99:352 (1954).

154. Roth, H. P., and E. A. Swenson, Physiological Studies of Irritant Aspects of Atmospheric Pollution, Report to the Los Angeles County Air Pollution Control District, Los Angeles, Calif. (1957).

155. Rounds, F. G., and H. W. Pearsall, Diesel Exhaust Odor (Its Evaluation and Relation to Exhaust Gas Composition), Vehicle Emissions (Selected S.A.E. Papers) 6:45 (1964)

156. Salem, H., and H. Cullumbine, Inhalation Toxicities of Some Aldehydes, Toxicol. Appl. Pharmacol. 2:183 (1960).

157. Sato, S., and R. J. Cvetanovic, Photooxidation of Butenes by Nitrogen Dioxide at Different Wave Lengths, Can. J. Chem. 36:1668 (1958).

158. Sato, S., and R. J. Cvetanovic, The Effect of Molecular Oxygen on the Reaction of Oxygen Atoms with cis-2-Pentene, Can. J. Chem. 37:953 (1959).

159. Sawicki, E., Spot Test Detection and Spectrophotometric Determination of Microgram Amounts of Aldehydes and Aldehyde-Yielding Compounds--A Review, Preprint, Presented at International Symposium on Microchemical Techniques, University Park, Pa. (Aug.13-18, 1961).

160. Sawicki, E., Airborne Carcinogens and Allied Compounds, Arch. Environ. Health 14:46 (1967).

161. Sawicki, E., and T. R. Hauser, Infrared Spectral Detection of Carboxylic Acids and Aldehydes in Air-Borne Particulates, Anal. Chem. 31:523 (1959).

162. Sawicki, E., and T. R. Hauser, Spot Test Detection and Colorimetric Determination of Aliphatic Aldehydes with 2-Hydrozinobenzothiazole: Application to Air Pollution, Presented at Air Pollution Symposium, 138th Meeting, American Chemical Society, New York (Sept. 1960).

163. Sawicki, E., and T. W. Stanley, Sensitive New Test for Aliphatic, Aromatic and Heterocyclic Aldehydes, Mikrochim. Acta p. 510 (1960).

164. Sawicki, E., T. R. Hauser, and S. McPherson, Spectrophotometric Determination of Formaldehyde and Formaldehyde-Releasing Compounds with Chromotropic Acid, 6-Amino-1-naphthol-3-sulfonic Acid (J Acid), and 6-Anilino-1-naphthol-3-sulfonic Acid (Phenyl J Acid), Anal. Chem.34:1460 (1962).

165. Sawicki, E., T. W. Stanley, and H. Johnson, Comparison of Spectrophotometric and Spectrophotofluorometric Methods for the Determination of Malonaldehyde, Anal. Chem. 35:199 (1963).

166. Sawicki, E., T. W. Stanley, and J. Pfaff, Spectrophotofluorimetric Determination of Formaldehyde and Acrolein with J-Acid, Comparison with Other Methods, Anal. Chim. Acta 28 (1963).

167. Sawicki, E., et al., The 3-Methyl-2-benzothiazolone Hydrazone Test. Sensitive New Methods for the Detection, Rapid Estimation, and Determination of Aliphatic Aldehydes, Anal. Chem. 33:92 (1961).

168. Sax, N. I., Dangerous Properties of Industrial Materials, 3rd ed. (New York: Reinhold, 1968).

169. Schuck, E. A., and G. J. Doyle, Photooxidation of Hydrocarbons in Mixtures Containing Oxides of Nitrogen and Sulfur Dioxide,Report No. 29, Air Pollution Foundation, San Marino, Calif. (1959).

170. Schuck, E. A., G. J. Doyle, and N. Endow, A Progress Report on the Photochemistry of Polluted Atmospheres, Stanford Research Institute (1960).

171. Schuck, E. A., H. W. Ford, and E. R. Stephens, Air Pollution Effects of Irradiated Automobile Exhaust As Related to Fuel Composition, Report No. 26, Air Pollution Foundation, San Marino, Calif. (Oct. 1958).

172. Schuck, E. A., E. R. Stephens, and J. T. Middleton, Eye Irritation Response at Low Concentrations of Irritants, Arch. Environ. Health 13:570 (1966).

173. Schumann, C. E., and C. W. Gruber, Motorist Exposures to Aldehydes from Diesel-Powered Buses, J. Air Pollution Control Assoc. 14:53 (1964).

174. Scott, W. E., and L. R. Reckner, Progress Report on Atmospheric Reaction Studies in the Los Angeles Basin November 15, 1968 to January 15, 1969, APRAC Project CAPA 7-68, Scott Research Laboratory (1969).

175. Scott, W. E., et al., Further Development in the Chemistry of the Atmosphere, Am. Petrol. Inst. 37:171 (1957).

176. 2nd Technical and Administrative Report on Air Pollution Control in Los Angeles County, 1950-51, Air Pollution Control District, County of Los Angeles.

177. Selected Methods for the Measurement of Air Pollutants, Public Health Service, Cincinnati, Ohio, Division of Air Pollution (May 1965).

178. Senderikhina, D. P., Determination of Acrolein in the Air, in Limits of Allowable Concentrations of Atmospheric Pollutants, Book 3 (1957).

179. Sheehy, J. P., W. C. Achinger, and R. A. Simon, Handbook of Air Pollution, U. S. Public Health Serv. Publ. 999-AP-44 (1965).

180. Sigsby, J. E., Jr., T. A. Bellar, and L. J. Leng, Dynamic Irradiation Chamber Tests of Automotive Exhaust Part II. Chemical Effects, J. Air Pollution Control Assoc. 12:522 (1962).

181. Sigsby, J. E., Jr., et al., Behavior of Simple Systems in a Large Irradiation Chamber, Presented at 145th National Meeting American Chemical Society, New York, (1963).

182. Sim, M., and R. E. Pattle, Effect of Possible Smog Irritants of Human Subjects, J. Am. Med. Assoc. 165(15): 1908 (1957).

183. Skog, E., A Toxicological Investigation of Lower Aliphatic Aldehydes, Acta Pharmacol. Toxicol. 6:299 (1950).

184. Skog, E., Anaesthetic and Haemolytic Action of Lower Aldehydes and Their Effect on Respiration and Blood Pressure, Acta Pharmacol. Toxicol. 8:275 (1952).

185. Smith, C. W. (Ed.), Acrolein (New York: Wiley, 1962).

186. Smith, W. S., Atmospheric Emissions from Fuel Oil Combustion, An Inventory Guide, Public Health Service (1962).

187. Smith, W. S., and C. W. Gruber, Atmospheric Emissions from Coal Combustion--An Inventory Guide, Public Health Service (1966).

188. The Smog Problem in Los Angeles County, Stanford Research Institute, Western Oil and Gas Association (1954).

189. Stenburg, R. L., _et al._, Effects of High Volatile Fuel on Incinerator Effluents, _J. Air Pollution Control Assoc._ _11_:376 (1961).

190. Stenburg, R. L., _et al._, Field Evaluation of Combustion Air Effects on Atmospheric Emissions from Municipal Incinerators, _J. Air Pollution Control Assoc._ _12_:83 (1962).

191. Stephens, E. R., in _Chemical Reactions in the Lower and Upper Atmosphere_, R. D. Cadle, Ed. (New York: Interscience, p.51, 1961).

192. Stephens, E. R., and W. E. Scott, Relative Reactivity of Various Hydrocarbons in Polluted Atmospheres, _Proc. A.P.I._ _42_:665 (1962).

193. Stephens, E. R., _et al._, Photochemical Reaction Products in Air Pollution, _Intern. J. Air Water Pollution_ _4_(1/2):79 (1961).

194. Stern, A. C., Present Status of Atmospheric Pollution in the United States, _Am. J. Public Health_ _50_(3):346 (1960).

195. Stern, A. C. (Ed.), _Air Pollution, I_, 2nd ed. (New York: Academic Press, 1968).

196. Stern, A. C. (Ed.), _Air Pollution, II_, 2nd ed. (New York: Academic Press, 1968).

197. Stern, A. C. (Ed.), _Air Pollution, III_, 2nd ed. (New York: Academic Press, 1968).

198. A Study of Air Pollution in the Interstate Region of Lewiston, Idaho and Clarkston, Washington, _U. S. Public Health Serv. Publ. 999-AP-8_ (Dec. 1964).

199. Taylor, O. C.,"Oxidant" Air Pollutants as Phototoxicants, California Univ., Riverside, Air Pollution Research Center Paper No. 64-91 (1964).

200. Taylor, O. C., _et al._, Effect of Air-borne Oxidants on Leaves of the Pinto Bean and Petunia, _Am. Soc. Hort. Sci._ _75_:435 (1960).

201. Technical Progress Report, Air Quality of Los Angeles County, vol. II, Air Pollution Control District County of Los Angeles (1961).

202. The Tenth Annual Report--1962. New York City Dept. of Air Pollution Control News 9(4) (Apr. 1963).

203. Thomas Register of American Manufacturers (New York: Thomas Publishing Co., 1968).

204. Threshold Limit Values for 1967, Adopted at the 29th Annual Meeting of the American Conference of Governmental Industrial Hygienists, Chicago, Ill. (May 1-2, 1967).

205. Tuesday, C. S., The Atmospheric Photooxidation of Transbutene-2 and Nitric Oxide, in Chemical Reactions in the Lower and Upper Atmosphere (New York: Interscience, pp. 1-49,1961).

206. U. S. Tariff Commission, Washington, D. C., personal communication (Apr. 1969).

207. Uzdina, I. L., Determination of Acrolein and of Formaldehyde in the Air, Hig. Truda 15:63 (1937).

208. Vandaveer, R. E., and C. G. Segeler, Partial Combustion of Gas with a Deficiency of Air, Ind. Eng. Chem. 37:816 (1945).

209. Walker, J. A., Influence of Gasoline Composition on the Constitution of Engine Exhaust (Part II of Atmospheric Pollution: A Survey of Some Aspects of the Emissions from Petrol-Engined Vehicles and Their Treatment), Brit. Techn. Council of the Motor and Petroleum Industries, England (Sept. 1965).

210. Walker, J. F., Formaldehyde, 3rd ed. (New York: Reinhold, 1964).

211. Walker, J. F., Formaldehyde, in Kirk-Othmer Encyclopedia of Chemical Technology, vol. 10 (New York: Interscience, pp. 77-99, 1966).

212. Wallach, A., Some Data and Observations on Combustion of Gaseous Effluents from Baked Lithograph Coatings, J. Air Pollution Control Assoc. 12(3):109 (1962).

213. Wayne, L. G., The Chemistry of Urban Atmospheres (Technical Progress Report —Volume III), Los Angeles County Air Pollution District, Calif. (Dec. 1962).

214. Weisburd, M. I., (Ed.), Air Pollution Control Field Operations Manual (A Guide for Inspection and Enforcement), Public Health Service, Washington, D.C., Division of Air Pollution (1962).

215. West, P. W., and B. Sen, Spectrophotometric Determination of Traces of Formaldehyde, Z. Anal. Chem. 153:177 (1956).

216. Wetmiller, R. S., and L. E. Endsley, Effect of Diesel Fuel on Exhaust Smoke and Odor, S.A.E. J. 50:509 (1942).

217. Williams, R. T., Detoxication Mechanisms, 2nd. ed. (New York: Wiley, 1959).

218. Wohlers, H. C., and G. B. Bell, Literature Review of Metropolitan Air Pollutant Concentration--Preparation, Sampling and Assay of Synthetic Atmosphere, Stanford Research Institute (1956).

219. Yant, W. P., et al., Acrolein as a Warning Agent for Detecting Leakage of Methyl Chloride from Refrigerators. U. S. Bur. of Mines Rept. Invest. 3027 (1930).

220. Yocum, J. E., G. M. Hein, and H. W. Nelson, Effluents from Backyard Incinerators, J. Air Pollution Control Assoc. 6:84 (1956).

221. Yunghans, R. S., and W. A. Munroe, Continuous Monitoring of Ambient Atmospheres with the Technicon Auto Analyzer, Presented at the Technicon Symposium, Automation in Analytical Chemistry, New York (Sept. 8, 1965).

APPENDIX

TABLE 10

PROPERTIES, TOXICITY, AND USES OF SOME ALDEHYDES[130]

Aldehyde	Properties	Toxicity	Uses
ALIPHATIC ALDEHYDES			
Formaldehyde HCHO	mp-92°C bp-19.5°C	Irritating to mucous membranes	
Acetaldehyde CH_3CHO	mp-123.5°C bp 21°C	Irritating to mucous membranes. General narcotic action. Large doses may cause death by respiratory paralysis. Symptoms of chronic intoxication resemble those of chronic alcoholism. LD_{50} orally in rats: 1.9 g/kg	In manufacture of paraldehyde, acetic acid, butanol, perfumes, flavors, aniline dyes, plastics, synthetic rubber; for silvering mirrors, hardening gelatin fibers
Propionaldehyde CH_3CH_2CHO	mp-81°C bp 49°C	May cause respiratory irritation. See acetaldehyde. LD_{50} orally in rats: 1.4 g/kg; lethal concentration for rats in air: 8,000 ppm	

(continued)

TABLE 10 (Continued)

PROPERTIES, TOXICITY, AND USES OF SOME ALDEHYDES

Aldehyde	Properties	Toxicity	Uses
Butyraldehyde $CH_3(CH_2)_2CHO$	mp-99°C bp 74.8°C	May act as irritant, narcotic Single dose LD_{50} orally in rats: 5.89 g/kg body wt	Chiefly in the manufacture of rubber accelerators, synthetic resins, solvents, plasticizers
Isobutyraldehyde $(CH_3)_2CHCHO$	mp-65.9°C bp 64°C	LD_{50} orally in rats: 3.7 g/kg Lethal concentration for rats in air: 16,000 ppm	In the synthesis of pantothenic acid, valine, leucine, cellulose esters, perfumes, flavors, plasticizers, resins, gasoline additives
n-Valeraldehyde $CH_3(CH_2)_3CHO$	bp 102-3°C	Has narcotic properties common to most aldehydes; is also a mild irritant	In flavoring compounds, resin chemistry, rubber accelerators
Isovaleraldehyde $(CH_3)_2CHCH_2CHO$	mp-51°C bp 92-93°C		In artificial flavors and perfumes
Pivalaldehyde $(CH_3)_3CCHO$	mp 6°C bp 75°C		

(continued)

TABLE 10 (Continued)

PROPERTIES, TOXICITY, AND USES OF SOME ALDEHYDES

Aldehyde	Properties	Toxicity	Uses
Caproaldehyde $CH_3(CH_2)_4CHO$	mp-56°C bp-128°C		
Enanthaldehyde $CH_3(CH_2)_5CHO$	mp-43°C bp 155°C		
Caprylaldehyde $CH_3(CH_2)_6CHO$	bp 163.4°C		
Pelargonaldehyde $CH_3(CH_2)_7CHO$	bp 185°C		
Capraldehyde $CH_3(CH_2)_8CHO$	bp 208°C		
Undecylaldehyde $CH_3(CH_2)_9CHO$	mp -4		

(continued)

TABLE 10 (Continued)

PROPERTIES, TOXICITY, AND USES OF SOME ALDEHYDES

Aldehyde	Properties	Toxicity	Uses
UNSATURATED ALDEHYDES			
Acrolein $CH_2{=}CHCHO$	mp-88°C bp 52.5°C	Irritates skin, mucous membranes. Vapors cause lacrimation. Sensitization, asthma have been reported. LD_{50} 30,000 μg/kg sc in mice	In manufacture of colloidal forms of metals; in making plastics, perfumes; as warning agent in methyl chloride refrigerant. Has been used in military poison gas mixtures. Used in organic syntheses
Crotonaldehyde $CH_3CH{=}CHCHO$	mp-76.5°C bp 104.0°C	Highly irritating to eyes, skin, and mucous membranes. Lethal concentrations for guinea pigs in air, 2,000 ppm	In manufacture of butyl alcohol, cutyraldehyde, quinaldine. As warning agent in fuel gases in locating breaks and leaks in pipes. Minor amounts are used in the manufacture of maleic acid, crotyl alcohol, butyl chloral hydrate, and in rubber accelerators. In organic syntheses; as solvent in purification of mineral oils; in manufacture of resins, rubber antioxidants, insecticides. In chemical warfare

(continued)

TABLE 10 (Continued)

PROPERTIES, TOXICITY, AND USES OF SOME ALDEHYDES

Aldehyde	Properties	Toxicity	Uses
Tiglaldehyde $CH_3CH{=}C(CH_3)CHO$	bp 102°C		
AROMATIC ALDEHYDES			
Benzaldehyde C_7H_6O	bp 179°C	Narcotic in high concentrations. May cause contact dermatitis. LD sc in rats, 5g/kg	In manufacture of dyes, perfumery, cinnamic and mandelic acids; as solvent; in flavors
o-Tolualdehyde C_8H_8O	bp 200-202°C		
m-Tolualdehyde C_8H_8O	bp 199°C		
p-Tolualdehyde C_8H_8O	bp 204-205°C		
Cinnamaldehyde $C_6H_5CH{=}CHCHO$	bp 246.0°C		In the flavor and perfume industry

(continued)

TABLE 10 (Continued)

PROPERTIES, TOXICITY, AND USES OF SOME ALDEHYDES

Aldehyde	Properties	Toxicity	Uses
HETEROCYCLIC ALDEHYDES			
Furfural $C_5H_4O_2$	bp 161.8°C	Irritates mucous membranes and acts on central nervous system. About one-third as toxic as formaldehyde. Causes lacrimation, inflammation of eyes, irritation of throat, headache. Chronic toxicity causes nervous disturbances, inflammation of eyes, photosensitivity, disturbance of vision. LD_{50} orally in dogs, 2.3 g/kg	In manufacture of furfural-phenol plastics such as Durite; in solvent refining of petroleum oils; in the preparation of pyromucic acid. As a solvent for nitrated cotton, cellulose acetate, and gums; in the manufacture of varnish; for accelerating vulcanization; as insecticide, fungicide, germacide; as reagent in analytical chemistry. In the syntheses of furan derivatives
POLYFUNCTIONAL ALDEHYDES			
Glyoxal $C_2H_2O_2$	mp 15°C bp 51°C	Moderately irritating to skin, mucous membranes. LD_{50} orally in rats, 2.0 g/kg	

(continued)

TABLE 10 (Continued)

PROPERTIES, TOXICITY, AND USES OF SOME ALDEHYDES

Aldehyde	Properties	Toxicity	Uses
Pyruvaldehyde $C_3H_4O_2$	bp 72°C		
Isophthalaldehyde $C_6H_4(CHO)_2$	mp 89°-90°C bp 245°-248°C		
Terephthalaldehyde $C_6H_4(CHO)_2$	mp 116°C bp 247°C		

APPENDIX

TABLE 11

TOXICITY OF ALDEHYDES TO ANIMALS VIA INHALATION[70]

Compound	Species	ppm	Time,hr	Mortality
SATURATED ALIPHATIC ALDEHYDES				
Formaldehyde	Rat	250	4	LC_{50}[a]
	Rat	815	0.5	LC_{50}
	Cat	650	8	LC_{50} approx
	Cat	200	3.5	All survived
Acetaldehyde	Rat	Sat vap[b]	2 min	LC_{100}
	Rat	16,000	4	0/6
	Rat	20,000	30 min	LC_{50}
	Cat	13,600	0.25	1/1
	Cat	4,100	3-5	0/1
	Cat	256	5	0/1
Propionaldehyde	Rat	8,000	4	5/6
	Rat	60,000	0.3	3/3
	Rat	26,000	0.5	LC_{50}
Ethoxypropionaldehyde	Rat	500	4	6/6
αβ-Dichloropropionaldehyde	Rat	Concd vap[c]	2 min	6/6
		16	4	4/6
n-Butyraldehyde	Rat	8,000	4	1/6
	Rat	60,000	0.5	LC_{50}
Isobutyraldehyde	Rat	8,000	4	1/6
β-Hydroxybutyraldehyde (aldol, acetaldol)	Rat	4,000	4	2/6
	Rat	Sat vap	0.5	No deaths
n-Valeraldehyde	Rat	48,000	1.2	3/3
	Rat	1,400	6	0/3
2-Methylbutyraldehyde	Rat	67,000	0.3	3/3
	Rat	3,800	6.0	0/3
	Rat	1,043	6.0	0/3
n-Hexaldehyde (hexanal)	Rat	Concd vap	4	0/6
	Rat	2,000	4	1/6

(continued)

APPENDIX

TABLE 11 (Continued)

TOXICITY OF ALDEHYDES TO ANIMALS VIA INHALATION[70]

Compound	Species	ppm	Time, hr	Mortality
SATURATED ALIPHATIC ALDEHYDES (Continued)				
2-Ethylbutyraldehyde	Rat	Concd vap	5 min	0/6
	Rat	8,000	1	5/6
2-Ethylhexylaldehyde (α-ethylcaproaldehyde)	Rat	25,000	13 min	3/3
	Rat	4,000	4	1/6
	Rat	2,000	23 min	3/3
	Rat	145	6	0/3
UNSATURATED ALIPHATIC ALDEHYDES				
Acrolein	Rat	8	4	1/6
	Cat	690-1,150	2	3/3
	Cat	18-92	3-4	0/2
	Cat	11	3-10	0/2
	Rat	130	30 min	LC_{50}
Methacrylaldehyde (Methacrolein)	Rat	250	4	5/6
2-Ethyl-3-propyl acrolein	Rat	Concd vap	8	0/6
Crotonaldehyde (β-methyl acrolein)	Rat	Concd vap	1 min	0/6
	Rat	1,400	30 min	LC_{50}
Methyl-β-ethyl acrolein (2-methyl-2-penten-1-al)	Rat	2,000	4	3/6
ALIPHATIC DIALDEHYDES				
Succinaldehyde (25% in H_2O)	Rat	Concd vap (ca. 15,000 μg/liter)	6	0/3
Hexa-2,4-dienal	Rat	2,000	4	1/6
3-Methyl glutaraldehyde	Rat	Concd vap	8	0/6
	Rat	Concd vap	6	0/3

(continued)

APPENDIX

TABLE 11 (Continued)

TOXICITY OF ALDEHYDES TO ANIMALS VIA INHALATION[70]

Compound	Species	ppm	Time, hr	Mortality
ALIPHATIC DIALDEHYDES (Continued)				
α-Hydroxyadipaldehyde	Rat	Concd vap	8	0/6

[a] LC = Lethal concentration.
[b] Sat vap = Saturated vapor.
[c] Concd vap = Concentrated vapor.

APPENDIX

TABLE 12

REPORTED ALDEHYDE EMISSION DATA[a]

Community	Emissions (tons/year)
Florida	
Dade County	1,737
Idaho	
Lewiston, Clarkston, and Washington area	169
Illinois	
Madison County	534
Monroe County	63
St. Clair County	811
Missouri	
Jefferson County	206
St. Charles County	89
St. Louis (city)	1,139
St. Louis County (excluding city of St. Louis	853
New York	
Chemung County	
Town	
Baldwin	1
Catlin	2
Chemung	2
Erin	1
Van Etten	2
Veteran	4
Rest of County	361
Total for Chemung County	373
Columbia County	
City	
Hudson	35
Town	
Ancram	3
Austerlitz	3
Canaan	3
Chatham	11
Claverack	15

(continued)

APPENDIX

TABLE 12 (Continued)

REPORTED ALDEHYDE EMISSION DATA

Community	Emissions (tons/year)
New York (continued)	
Columbia County (continued)	
Town (continued)	
Clermont	2
Copake	4
Gallatin	2
Germantown	7
Ghent	13
Greenport	209
Hillsdale	4
Kinderhook	13
Livingston	4
New Lebanon	4
Stockport	6
Stuyvesant	4
Taghkanic	1
Village[b]	
Chatham	6
Philmont	7
Kinderhook	2
Valatie	4
Total for Columbia County	343
Dutchess County	
City	
Beacon	64
Poughkeepsie	120
Town	
Amenia	37
Beekman	4
Clinton	5
Dover	30
East Fishkill	20
Fishkill	26
Hyde Park	45
La Grange	24
Milan	3
Northeast	14
Pawling	16
Pine Plains	6
Pleasant Valley	15

(continued)

APPENDIX

TABLE 12 (Continued)

REPORTED ALDEHYDE EMISSION DATA

Community	Emissions (tons/year)
New York (continued)	
Dutchess County (continued)	
Town (continued)	
Poughkeepsie	168
Red Hook	24
Rhinebeck	18
Stanford	5
Union Vale	3
Wappinger	33
Washington	15
Village[b]	
Wappingers Falls	18
Fishkill	2
Millerton	2
Pawling	5
Red Hook	5
Tivoli	3
Rhinebeck	6
Millbrook	4
Total for Dutchess County	695
Erie County	
City	
Buffalo	7,225
Lackawanna	272
Tonawanda	138
Town	
Amherst	227
Cheektowaga	351
Hamburg	205
Tonawanda	3,776
West Seneca	160
Alden	40
Aurora	36
Boston	14
Brant	11
Clarence	66
Colden	12
Collins	50
Concord	20
Eden	26

(continued)

APPENDIX

TABLE 12 (Continued)

REPORTED ALDEHYDE EMISSION DATA

Community	Emissions (tons/year)
New York (continued)	
Erie County (continued)	
Town (continued)	
Elma	28
Evans	43
Holland	13
Lancaster	34
Marilla	8
Newstead	25
North Collins	11
Orchard Park	26
Sardinia	9
Wales	8
Village[b]	
Blasdell	23
Depew	70
Hamburg	33
Kenmore	97
Lancaster	62
Sloan	34
Williamsville	45
Akron	35
Alden	12
Angola	13
East Aurora	34
Farnham	3
Gowanda	5
Grand Island	32
North Collins	10
Orchard Park	16
Springville	24
Greene County	
Town	
Ashland	1
Athens	10
Cairo	11
Catskill	472
Coxsackie	20
Durham	8
Greenville	10
Hunter	9

(continued)

TABLE 12 (Continued)

REPORTED ALDEHYDE EMISSION DATA

Community	Emissions (tons/year)
New York (continued)	
Greene County (continued)	
Town (continued)	
Jewett	1
Lexington	2
New Baltimore	7
Prattsville	3
Windham	7
Village[b]	
Athens	6
Catskill	20
Coxsackie	8
Hunter	2
Tannersville	2
Total for Greene County	561
Rockland County	
Town	
Clarkstown	100
Haverstraw	78
Orangetown	156
Ramapo	120
Stoney Point	203
Village[b]	
Stoney Point	203
Spring Valley	21
Upper Nyack	5
Haverstraw	37
West Haverstraw	15
Grandview-on-Hudson	1
Nyack	18
Piermont	14
South Nyack	8
Hillburn	29
Suffern	16
Sloatsburg	8
New Square	1
Total for Rockland County	657

(continued)

APPENDIX

TABLE 12 (Continued)

REPORTED ALDEHYDE EMISSION DATA

Community	Emissions (tons/year)
New York (continued)	
Ulster County	
City	
Kingston	280
Town	
Esopus	31
Gardiner	5
Hardenburgh	1
Hurley	14
Kingston	2
Lloyd	21
Marbletown	11
Marlborough	15
New Paltz	18
Olive	5
Plattekill	12
Rochester	9
Rosendale	24
Saugerties	37
Shandaken	9
Shawangunk	14
Ulster	36
Wawarsing	36
Woodstock	25
Village[b]	
New Paltz	10
Rosendale	2
Saugerties	10
Ellenville	19
Total for Ulster County	605
Westchester County	
City	
White Plains	131
Peekskill	98
Mount Vernon	136
New Rochelle	164
Yonkers	396
Rye	37

(continued)

APPENDIX

TABLE 12 (Continued)

REPORTED ALDEHYDE EMISSION DATA

Community	Emissions (tons/year)
New York (continued)	
Westchester County (continued)	
Town	
Bedford	84
Cortlandt	135
Eastchester	128
Greenburg	207
Harrison	77
Lewisboro	37
Mamaroneck	66
Mount Pleasant	129
New Castle	70
North Salem	42
Ossining	72
Pelham	30
Pound Ridge	24
Rye	110
Scarsdale	43
Somers	52
Yorktown	84
Village[b]	
Ossining	42
Port Chester	75
Mamaroneck	40
Scarsdale	43
Mount Kisco	22
Croton	40
Bronxville	13
Tuckahoe	20
Ardsley	10
Dobbs Ferry	15
Hastings	26
Irvington	12
Tarrytown	25
Larchmont	12
Briarcliff Manor	17
North Tarrytown	29
Pleasantville	20
North Pelham	8
Pelham	4

(continued)

APPENDIX

TABLE 12 (Continued)

REPORTED ALDEHYDE EMISSION DATA

Community	Emissions (tons/year)
New York (continued)	
Westchester County (continued)	
Village (continued)	
Pelham Manor	16
Elmsford	14
Buchanan	27
Total for Westchester County	2,400

[a] These data compiled from References 1-4,97,98,121.
[b] Village data included in appropriate towns.

APPENDIX

TABLE 13

U.S. PRODUCTION OF FORMALDEHYDE, 1958-68[206]

Date	Production (Thousands of Pounds)	Quantity of Sales (Thousands of Pounds)	Value of Sales (Thousands of Dollars)
1958	1,358,444	542,142	19,286
1959	1,750,218	685,986	22,965
1960	1,872,448	678,262	22,649
1961	1,752,395	723,254	23,633
1962	2,398,067	835,572	26,474
1963	2,537,236	919,763	27,799
1964	2,839,884	1,067,340	27,973
1965	3,106,572	1,189,434	30,199
1966	3,712,568	1,359,981	36,751
1967	3,707,093	1,289,720	33,633
1968	4,099,586		

APPENDIX

TABLE 14

PRINCIPAL U.S. MANUFACTURERS OF ACROLEIN AND FORMALDEHYDE[203]

Manufacturer	Location
ACROLEIN (and its derivatives)	
Shell Chemical Co.	New York, N.Y.
Union Carbide Corp. Chemicals Div.	New York, N.Y.
FORMALDEHYDE (and its derivatives)	
Allied Chemical Corp. Nitrogen Div.	New York, N.Y.
Baker, J. T., Chemical Co.	Phillipsburg, N.J.
Big Ben Chemicals & Solvents, Inc.	Chicago, Ill.
Borden Chemical Co.	New York, N.Y.
Celanese Chemical Co.	New York, N.Y.
Commerce Chemical Corp.	New York, N.Y.
Commercial Solvents Corp.	New York, N.Y.
Degussa Inc. Chemical Div.	Kearny, N.J.
du Pont, E. I., de Nemours & Co., Inc.	Wilmington, Del.
General Aniline & Film Corp.	New York, N.Y.
Georgia-Pacific Corp.	Portland, Ore.
Globe Chemical Co., Inc.	Cincinnati, Ohio
Hachik Bleach Co.	Philadelphia, Pa.
Harshaw Chemical Co.	Cleveland, Ohio
Haviland Products Co.	Grand Rapids, Mich.
Hercules Inc.	Wilmington, Del.
Hubbard Hall Chemical Co.	Waterbury, Conn.
King, E. & F., & Co., Inc.	Norwood, Mass.
Kraft Chemical Co.	Chicago, Ill.
Lewis, John D., Inc.	Providence, R.I.
Mallinckrodt Chemical Works	St. Louis, Mo.
McKesson & Robbins, Inc.	New York, N.Y.
Merck & Co., Inc.	Rahway, N.J.
Monsanto Co. Plastics Div.	Springfield, Mass.
Nicholson & Co.	Cambridge, Mass.
Nitine, Inc.	Whippany, N.J.
Octagon Process, Inc.	Edgewater, N.J.
Philipp Brothers Chemicals, Inc.	New York, N.Y.
Reichhold Chemicals Inc.	White Plains, N.Y.
Riverside Chemical Co., Inc.	North Tonawanda, N.Y.
Robinson Brothers Chemicals, Inc.	Brooklyn, N.Y.
Scholle Chemical Corp.	Northlake, Ill.
Seaway Chemical Corp.	Buffalo, N.Y.
Siegel Chemical Corp.	Brooklyn, N.Y.
Tenneco Chemicals, Inc.	New York, N.Y.
Treys, Geo. I., Co.	Cooks Falls, N.Y.
Union Carbide Corp. Chemicals Div.	New York, N.Y.
Washing Chemical Corp.	Lodi, N.J.

APPENDIX

TABLE 15

USES OF FORMALDEHYDE IN THE UNITED STATES, 1964[211]

Use	Percentage of Formaldehyde Consumption
Resins	
Phenolic	20.1
Urea	20.8
Melamine	6.0
Acetal	4.0
	50.9
Urea-formaldehyde concentrates	
Industrial	7.6
Agricultrual	2.8
	10.4
Special chemicals	
Hexamethylenetetramine	5.7
Pentacrythritol	8.2
Ethylene glycol	14.3
Sequestering agents	1.4
	29.6
Other uses	9.1

APPENDIX

TABLE 16

YIELDS OF ALDEHYDES VIA PHOTOCHEMICAL OXIDATION OF HYDROCARBON-NITROGEN OXIDE MIXTURES[11]

Hydrocarbon	Moles/mole of initial hydrocarbon			
	Formaldehyde	Acetaldehyde	Acrolein	Total or Other Aldehydes
Ethylene	0.35,0.45 0.32,0.45	0.01		
Propylene	0.40,0.45	0.4,0.15-0.2		
1-Butene	0.45,0.4			0.9,0.5
Isobutene	0.7,0.6 0.3-0.45,0.6 0.6,0.5-0.7	0.01		
Trans-2-butene	0.35,0.35	1.40,1.5 0.9-1.2		
Cis-2-butene		0.9,0.8-1.0		1.0,0.9
1,3-Butadiene	0.6,0.6,0.5	0.01	0.55,0.25 0.2	
1-Pentene	0.55			0.4
2-Methyl-2-butene	0.5,0.3	0.75,0.4-0.5		
1,3-Pentadiene	0.65		0.35	1.3
2-Methyl-1,3-pentadiene	0.55		0.4	0.9
Cis-3-hexene				1.0,0.9-1.0, 0.9-1.0
2,3-Dimethyl-2-butene	0.25			
Cyclohexene	0.4			
2,3-Dimethyl-1,3-butadiene	0.65			1.3
3-Heptene	0.8			1.2
Toluene				0.11
p-Xylene	0.15			0.26
o-Xylene				0.22
m-Xylene	0.15			0.25,0.3
1,3,5-Trimethylbenzene	0.15			0.6,0.3,0.4
1,2,4,5-Tetramethylbenzene				0.45

TABLE 17

REPORTED ALDEHYDE EMISSIONS FROM AUTOMOBILE ENGINES

Source	Aldehydes (as Formaldehyde) ($\mu g/m^3$)	Formaldehyde ($\mu g/m^3$)	Acrolein ($\mu g/m^3$)	Ref.
Automobile, general				
(1 gal gasoline = 6.25 lb)	3.4 lb/1,000 gal gasoline			218
	4 lb/1,000 gal gasoline			45
	10 lb/1,000 gal gasoline			93
	17.5 lb/1,000 gal gasoline			50
	18.7 lb/1,000 gal gasoline			119
Cruise	3.3 lb/1,000 gal gasoline			176
Acceleration or deceleration	7.1 lb/1,000 gal gasoline			176
Automobile, general				
Idle	18,000			209
Acceleration	56,400			209
Deceleration	238,800			209
Fuel				
House Brand (Mid-continent area regular grade)				
Idle	58,800	24,000		95,96
40 mph cruise	184,800	99,600		95,96
50 mph cruise	114,000	48,000		95,96
60 mph cruise	112,800	46,800		95,96
40 mph 2/3 max torque	115,200	39,600		95,96
Acceleration (15 to 60 mph in 25 sec)	72,000-142,800	36,000-46,800		95,96
Deceleration (50 to 15 mph in 25 sec)	289,000-967,200	106,800-282,000		95,96
West Coast regular brand (WOGA No. 3)				
Idle	60,000	34,800		95,96

(continued)

TABLE 17 (Continued)

REPORTED ALDEHYDE EMISSIONS FROM AUTOMOBILE ENGINES

Source	Aldehydes (as Formaldehyde) ($\mu g/m^3$)	Formaldehyde ($\mu g/m^3$)	Acrolein ($\mu g/m^3$)	Ref.
40 mph cruise	140,400	80,400		95,96
60 mph cruise	114,000	49,200		95,96
40 mph 2/3 max torque	61,200	36,000		95,96
West Coast aromatic (WOGA No. 2A)				
Idle	88,800	19,200		95,96
40 mph cruise	180,000	54,000		95,96
60 mph cruise	106,800	39,600		95,96
40 mph 2/3 max torque	129,600	21,600		95,96
West Coast paraffinic (WOGA No. 2P)				
Idle	62,400	32,400		95,96
40 mph cruise	163,200	97,200		95,96
60 mph cruise	128,400	51,600		95,96
40 mph 2/3 max torque	98,400	57,600		95,96
Engine mode				
Idle	100,000			119
	105,600			139
	72,000			150
Cruise	200,000			119
	316,800			139
	168,000			150
Cruise, 30 mph		36,000	21,250	22,51
Cruise, 15 mph	93,600	34,800		67
40 mph	105,600	54,000		67
60 mph	114,000	52,800		67
Deceleration (coasting)			17,500	22,51

(continued)

TABLE 17 (Continued)

REPORTED ALDEHYDE EMISSIONS FROM AUTOMOBILE ENGINES

Source	Aldehydes (as Formaldehyde) ($\mu g/m^3$)	Formaldehyde ($\mu g/m^3$)	Acrolein ($\mu g/m^3$)	Ref.
Gasoline, 707 in^3 (44-passenger coach)				
Idle		36,000; 0.048 SCFH*		66,155
Acceleration		19,200; 0.157 SCFH		66,155
Cruise, 30 mph		8,400; 0.048 SCFH		66,155
Deceleration		343,200; 0.756 SCFH		66,155
Chicago Transit Driving Pattern		0.17 SCFH		66,155
Propane, 477 in^3 (50-passenger coach)				
Idle		36,000; 0.025 SCFH		66,155
Acceleration		21,600; 0.157 SCFH		66,155
Cruise, 30 mph		27,600; 0.123 SCFH		66,155
Deceleration		206,400; 0.247 SCFH		66,155
Chicago Transit Driving Pattern		0.11 SCFH		66,155

*Standard cubic feet per hour at 60°C and 760 mm.

APPENDIX

TABLE 18

REPORTED ALDEHYDE EMISSIONS FROM DIESEL ENGINES

Source	Aldehydes (as Formaldehyde) ($\mu g/m^3$)	Formaldehyde ($\mu g/m^3$)	Acrolein ($\mu g/m^3$)	Ref.
Diesel engine	2.5 lb/1,000 lb fuel			108
Diesel engine	10 lb/1,000 gal burned			218
Diesel engine	16 lb/1,000 gal burned			93
Diesel, 2 cycle, No. 2 fuel				
Idle		13,200; 192,000[a]		197
No load		8,760; 84,240[a]		197
½ load		9,720; 40,200[a]		197
Full load		15,600; 38,400[a]		197
Diesel, 2-cycle, 426 in^3, full load, 2,000 rpm	114,000	51,600		102
Diesel, 2 cycle, 6 cylinder, 220 hp, supercharged, No. 2 fuel				
600 rpm, 0 hp		6,240	11,175	114
1,000 rpm, 50 hp		4,056	2,100	114
1,200 rpm, 100 hp		3,567	3,500	114
1,600 rpm, 150 hp		12,240	7,425	114
2,200 rpm, 200 hp		21,720	7,800	114

(continued)

TABLE 18 (Continued)

REPORTED ALDEHYDE EMISSIONS FROM DIESEL ENGINES

Source	Aldehydes (as Formaldehyde) ($\mu g/m^3$)	Formaldehyde ($\mu g/m^3$)	Acrolein ($\mu g/m^3$)	Ref.
Diesel, 2 cycle, No. 2 fuel				
500 rpm, no load		12,720; 0.027 lb/gal fuel	10,500; 0.020 lb/gal fuel	146
1,200 rpm, ¼ load		5,520; 0.004 lb/gal fuel	3,500; 0.002 lb/gal fuel	146
1,600 rpm, full load		22,800; 0.005 lb/gal fuel	12,750; 0.003 lb/gal fuel	146
Diesel, 2 cycle, 426 in^3 (45-passenger coach):				
Idle		10,800; 0.073 SCFH[b]		66,155
Acceleration		20,400; 0.509 SCFH		66,155
Cruise, 30 mph		13,200; 0.203 SCFH		66,155
Deceleration		34,800; 0.541 SCFH		66,155
Chicato Transit Driving Pattern		0.24 SCFH		66,155
Diesel, 4 cycle, No. 2 fuel				
Idle		8,160; 130,800[a]		197
No load		2,160; 26,160[a]		197
½ load		8,160; 23,400[a]		197
Full load		5,160; 7,200[a]		197

(continued)

TABLE 18 (Continued)

REPORTED ALDEHYDE EMISSIONS FROM DIESEL ENGINES

Source	Aldehydes (as Formaldehyde) ($\mu g/m^3$)	Formaldehyde ($\mu g/m^3$)	Acrolein ($\mu g/m^3$)	Ref.
Diesel, 4 cycle 673 in^3				
Full load				
2,000 rpm		5,040		102
1,000 rpm		9,240		102
Half load				
2,000 rpm		4,800		102
1,000 rpm		4,800		102
Diesel, 4 cycle, 6 cylinder, 300 hp turbosupercharged, No. 2 fuel, club propeller as a load				
700 rpm		12,600		114
800 rpm		23,880	22,200	114
1,050 rpm		18,120	40,500	114
1,300 rpm		16,800	42,500	114
1,520 rpm		20,160	33,500	114
1,685 rpm		32,040		114
1,780 rpm		25,080	43,500	114
Diesel, 4 cycle, No. 2 fuel				
740 rpm, no load	57,600	31,200; 0.036 lb/gal fuel	13,000	146

(continued)

TABLE 18 (Continued)

REPORTED ALDEHYDE EMISSIONS FROM DIESEL ENGINES

Source	Aldehydes (as Formaldehyde) (μg/m^3)	Formaldehyde (μg/m^3)	Acrolein (μg/m^3)	Ref.
1,200 rpm, no load	49,200	39,600	12,500	146
¼ load	21,600	14,400; 0.006 lb/gal fuel	4,500	146
½ load	28,800	21,600	3,500	146
3/4 load	26,400	21,600	4,500	146
Full load	38,400	31,200; 0.005 lb/gal fuel	2,000	146
1,500 rpm, no load	50,400	33,600	13,750	146
¼ load	34,800	21,600	3,500	146
½ load	32,400	20,400	4,250	146
3/4 load	31,200	22,800	4,750	146
Full load	55,200	37,200	7,500	146
1,800 rpm, no load	48,000	39,600	12,500	146
¼ load	34,800	24,000	8,000	146
½ load	28,800	18,000	6,500	146
3/4 load	44,400	36,000	5,750	146
Full load	67,200	48,000	8,250	146
Diesel, 1959 Plymouth Savoy, Perkins P4C, 4 cylinder, 4 stroke				
Idle	48,000			102
Acceleration	7,200			102

(continued)

APPENDIX

TABLE 18 (Continued)

REPORTED ALDEHYDE EMISSIONS FROM DIESEL ENGINES

Source	Aldehydes (as Formaldehyde) (μg/m³)	Formaldehyde (μg/m³)	Acrolein (μg/m³)	Ref.
Diesel, 1959 Mercedes-Benz 1900				
Idle	48,000			102
Acceleration	20,400			102
Diesel, mine locomotive				
Idle	54,000			37,102
Upgrade haul	31,200			
Downgrade haul	69,600			

[a] Data normalized to $(CO+CO_2)$ = to 15 percent to correct for dilution by excess air.

[b] Standard cubic feet per hour at 60°C and 760 mm.

TABLE 19

REPORTED ALDEHYDE EMISSIONS FROM COMMERCIAL AIRCRAFT

Source	Aldehydes (as Formaldehyde)	Formaldehyde	Ref.
Jet Aircraft (Los Angeles County) 1960	0.1 ton/day		78
1965 (projected)	0.6 ton/day		78
Operations[a] (1960), total (below 3,500 ft.)	230 lb/day		78
Taxiing	91 lb/day		78
Take off	16 lb/day		78
Climb-out	15 lb/day		78
Approach	83 lb/day		78
Landing	25 lb/day		78
Aircraft, jet turbine (estimated 15,000 lb thrust)			
Idle	6,000 μg/m^3, 2 lb/hr		197
Cruise	1,200 μg/m^3, 1.5 lb/hr		197
Take off	Trace		197
Aircraft, total operations (below 3,500 ft.)			
Jet, 4 engines	4 lb/flight,[b] 6 lb/1,000 gal fuel		97,122
Turboprop, 2 engines	0.3 lb/flight, 5 lb/1,000 gal fuel		97,122
Turboprop, 4 engines	1.1 lb/flight		97,122
Piston engine, 2 engines	0.2 lb/flight, 5 lb/1,000 gal fuel		97,122
Piston engine, 4 engines	0.5 lb/flight		97,122

(continued)

TABLE 19 (Continued)

REPORTED ALDEHYDE EMISSIONS FROM COMMERCIAL AIRCRAFT

Source	Aldehydes (as Formaldehyde)	Formaldehyde	Ref.
Aircraft, turboprop, T-56			
Departure[c]	0.14 lb		117
Arrival[c]	0.13 lb		117
100% power (take off)	4,920 $\mu g/m^3$, 0.5 lb/hr	1,320 $\mu g/m^3$, 0.2 lb/hr	117
75% power (cruise and approach)	2,400 $\mu g/m^3$, 0.2 lb/hr	2,280 $\mu g/m^3$, 0.2 lb/hr	117
65% power (idle)	5,760 $\mu g/m^3$, 0.3 lb/hr	4,200 $\mu g/m^3$, 0.2 lb/hr	117
Aircraft, conventional jet, J-57			
Departure[c]	0.19 lb		117
Arrival[c]	0.25 lb		117
100% power (take off)	960 $\mu g/m^3$, 0.5 lb/hr	600 $\mu g/m^3$, 0.4 lb/hr	117
75% power (cruise)	960 $\mu g/m^3$, 0.4 lb/hr	600 $\mu g/m^3$, 0.3 lb/hr	117
65% power (idle)	3,000 $\mu g/m^3$, 0.4 lb/hr	2,800 $\mu g/m^3$, 0.4 lb/hr	117
Aircraft, fan-jet, TF-33			
Departure[c]	2.04 lb		117
Arrival[c]	2.62 lb		117
100% power (take off)	720 $\mu g/m^3$, 0.4 lb/hr		117
75% power (approach	360 $\mu g/m^3$, 0.3 lb/hr		117
65% power (idle)	25,200 $\mu g/m^3$, 0.4 lb/hr		117

[a] Based on 40 arrivals and departures per day.

[b] Flight defined as a combination of take off and landing.

[c] Based on 4 engines, taxiing time, plus take off and climb-out or approach and landing.

APPENDIX

TABLE 20

REPORTED ALDEHYDE EMISSIONS FROM COMBUSTION OF COAL

Source	Aldehydes (as Formaldehyde)	Formaldehyde	Ref.
Bituminous (27,200,000 BTU/ton)	2 lb/ton		93
Anthracite (25,200,000 BTU/ton)	1 lb/ton		93
Bituminous from pulverized fuel of cyclone furnaces	<0.01 lb/ton		140
Flue gas	60-300 μg/m^3		140
Coal-burning power plants,* full load			55,138, 187
Before ash-collecting			
Vertical boiler		300 μg/m^3	"
Corner boiler		204 μg/m^3	"
Front-wall boiler		168 μg/m^3	"
Spreader-stoker boiler		72 μg/m^3	"
Cyclone boiler		204 μg/m^3	"
Horizontally opposed boiler		120 μg/m^3	"
After ash-collecting			
Vertical boiler		144 μg/m^3	"
Front-wall boiler		144 μg/m^3	"
Spreader-stoker boiler		96 μg/m^3	"
Cyclone boiler		120 μg/m^3	"
Horizontally opposed boiler		84 μg/m^3	"
Power plants	0.005 lb/ton		122
Industrial	0.005 lb/ton		122
Domestic and commercial	0.005 lb/ton		122

*1,200 μg/m^3 ≅ 1 ppm ≅ 10^{-3} lb/10^{-6} BTU.

TABLE 21

REPORTED ALDEHYDE EMISSIONS FROM COMBUSTION OF FUEL OIL

Source	μg/m³	ppm	lb/hr	lb/ 1,000 lb	Ref.
Fuel Oil					
Distillate (~7 lb/gal)*				.28 (0-2.07)	93,218
Residual (~8 lb/gal)				.14	93,218
No. 2				1.3	93,218
Small sources (1,000 hp or less) (~8 lb/gal)					
Extreme range	0-216,000	0-180		0-3.3	186
Usual range	0-39,600	0-33		0-0.6	186
Large sources (1,000 hp or more) (~8 lb/gal)					
Extreme range	0-80,400	0-67		0-1.2	186
Kerosene burners					
Fan-assisted pot (20,000 kcal/hr output)					
Good condition	4,800	4			197
Bad condition	16,800	14			197
Wallflame (10,000 kcal/hr output)					
Good condition	3,600	3			197
Bad condition	30,000	25			197

(continued)

TABLE 21 (Continued)

REPORTED ALDEHYDE EMISSIONS FROM COMBUSTION OF FUEL OIL

Source	μg/m³	ppm	lb/hr	lb/ 1,000 lb	Ref.
Pressure atomizing (10,500 kcal/hr output)					
Good condition	3,600	3			197
Bad condition	12,000	10			197
Fuel oil, No. 1					
Scotch marine boiler, 150 hp	6,000	5	0.04		44
Ceramic kiln	4,200	3.5	0.0037		44
Ceramic kiln	4,080	3.4	0.020		44
Fuel oil, heavy					
Fire tube boiler, 120 hp	8,400	7	0.05		44
Scotch marine boiler, 125 hp	10,800	9	0.08		44
Water tube boiler, 245 hp	9,600	8	0.2		44
Water tube boiler, 425 hp	4,800	4	0.2		44
Water tube boiler, 460 hp	8,400	7	0.2		44
Water tube boiler, 500 hp	20,400	17	1.0		44
Water tube boiler, 580 hp	10,200	8.5	0.12		44
Water tube boiler, 870 hp	57,600	48	1.8		44
Fuel oil, No. 2					
Fire tube boiler, 60 hp	10,800	9	0.017		44
Fire tube boiler, 300 hp	7,200	6	0.08		44
Scotch marine boiler, 200 hp	62,400	52	0.50		44
Scotch marine boiler, 350 hp	3,600	3	0.06		44
Water tube boiler, 100 hp	6,000	5	0.013		44
Water tube boiler, 200 hp	9,600	8	0.04		44
Water tube boiler, 245 hp	8,400	7	0.04		44
Oil heater	13,200	11	0.015		44

*1,000 lb ≅ 140 gal or 84 gal ≃ 12 X 10^6 BTU.

TABLE 22. REPORTED ALDEHYDE EMISSIONS FROM NATURAL GAS COMBUSTION

Source	Aldehyde	Ref.
Natural gas-fired appliances and industrial and commercial equipment		
Bunsen burner	2,400 $\mu g/m^3$	197
Oven range	13,200 $\mu g/m^3$; 0.02 lb/10^6 BTU	197
Water heater, 100 gal	9,600 $\mu g/m^3$; 0.01 lb/10^6 BTU	197
Floor furnace	3,600 $\mu g/m^3$; 0.005 lb/10^6 BTU	197
Steam boiler (10^7 BTU/hr) (low fire)	6,000 $\mu g/m^3$; 0.01 lb/10^6 BTU	197
Industrial burners	58,800 $\mu g/m^3$	197
Boilers and process heaters	0.0028 lb/10^6 BTU	197
Scotch marine boilers	2,400-8,400 $\mu g/m^3$	197
Fire tube boilers	4,800 $\mu g/m^3$	197
Water tube boilers	3,600-13,200 $\mu g/m^3$	197
75 gal water heater	2,400 $\mu g/m^3$	197
Space heater	2,400 $\mu g/m^3$	197
Bake oven	7,200 $\mu g/m^3$	197
Industrial oven, indirect	3,600-7,200 $\mu g/m^3$	197
Ceramic kilns, indirect	2,400-8,400 $\mu g/m^3$	197
Natural gas combustion (12 X 10^6 BTU ≅ 12,000 ft^3 gas)	0.7 lb/12 X 10^6 BTU	218
Natural gas combustion (1,000 lb gas ≅ 21,785 ft^3 or 23 X 10^6 BTU)	1 lb/1,000 lb gas	50,119, 188
Natural gas (~0.045 lb/ft^3; 1,000 BTU/ft^3)	10 lb/10^6 ft^3 gas	93
Propane (~0.117 lb/ft^3; 2,522 BTU/ft^3)	26 lb/10^6 ft^3 gas	93
Butane (~0.154 lb/ft^3; 3,261 BTU/ft^3)	34 lb/10^6 ft^3 gas	93
Power plants	0.02 lb/1,000 lb gas; 1 lb/10^6 ft^3 gas	214 214
Industrial	0.1 lb/1,000 lb gas; 2 lb/10^6 ft^3 gas	214 214
Domestic and commercial	0.25 lb/1,000 lb gas	214

APPENDIX

TABLE 23

REPORTED ALDEHYDE EMISSIONS FROM INCINERATORS

Source	Aldehydes (as Formaldehyde)	Ref.
Domestic incinerators		
AGA prototype, shredded paper	9,600-25,200 $\mu g/m^3$; 0.9-2.3 lb/ton	197
AGA prototype, USASI[a] domestic wastes	9,600 $\mu g/m^3$; 0.8 lb/ton	197
AGA prototype, other refuse mixtures	20,400-26,400 $\mu g/m^3$; 1.2-3.1 lb/ ton	197
New manufacturers' units, shredded paper	4,800-80,400 $\mu g/m^3$; 0.17-15.9 lb/ton	197
New manufacturers' units, USASI domestic wastes	30,000-48,000 $\mu g/m^3$	197
Older units, shredded paper	28,800-57,600 $\mu g/m^3$	197
Older units, USASI domestic wastes	6,000-36,000 $\mu g/m^3$; 5-6 lb/ton	197
Domestic incinerator	4.0 lb/ton refuse	120
Domestic incinerator	1.4 lb/ton refuse	120
Domestic, single chamber		
Without auxiliary gas burning	6 lb/ton refuse	97,122
With auxiliary gas burning	2 lb/ton refuse	97,122
Municipal incinerators		
Glendale, Calif., with scrubber	1,200-12,000 $\mu g/m^3$	197
Glendale, Calif., without scrubber	1,200-26,400 $\mu g/m^3$	197
Alhambra, Calif., with spray chamber	58,800 $\mu g/m^3$; 1.1 lb/ton	197
Three units in Calif. with scrubber	10,800-32,400 $\mu g/m^3$	197
Three units in Calif. without scrubber	1,200-56,400 $\mu g/m^3$	197
Incinerator, municipal	1.4 lb/ton refuse	120
Incinerator, large and/or multistage	1.1 lb/ton refuse	120
Incinerator, multichamber	1.1 lb/ton refuse	122
Other incinerators		
Single chamber	0.03-2.7 lb/ton	197
Wood waste	40,800 $\mu g/m^3$; 1.8 lb/ton	197
Backyard (Battelle), paper and trimmings	912,000 $\mu g/m^3$; 29 lb/ton	197
Backyard, 6 ft^3, paper	58,800 $\mu g/m^3$; 2.1 lb/ton	197
Backyard, 6 ft^3, trimmings	122,400 $\mu g/m^3$; 5.7 lb/ton	197

(continued)

TABLE 23 (Continued)

REPORTED ALDEHYDE EMISSIONS FROM INCINERATORS

Source	Aldehydes (as Formaldehyde)	Ref.
Other incinerators (continued)		
Backyard, 3 ft^3, mixed rubbish	5.1 lb/ton	197
Incinerator, apartment, flue-fed	2.5-7.8 lb/ton refuse	99
Incinerators	129,600-984,000 $\mu g/m^3$	98
Commercial and domestic, small and/or single-stage	3 lb/ton refuse (0.1-4.5 lb/ton)	93
Industrial and commercial, single chamber	5-64 lb/ton refuse	97
Multiple chamber	0.3 lb/ton refuse (0.14-0.85 lb/ton)	60,97, 122
Apartment, flue-fed	5 lb/ton refuse	122
Multiple chamber, experimental (asphalt, felt roofing, and newspaper)	0.008-0.32 lb/ton material; ~120-1,200 $\mu g/m^3$[b]	189 189
Incinerator, automobile, afterburner on	3,600 $\mu g/m^3$	189
Afterburner off	19,200 $\mu g/m^3$	189
Incinerator, pathological waste		
Placental tissue in newspaper	0.985 lb/ton, 0.013 lb/ hr	60
Dogs freshly killed	0.617 lb/ton, 0.033 lb/hr	60

[a] United States of America Standards Institute.

[b] Figures given are range of formaldehyde.

TABLE 24

ALDEHYDE EMISSIONS FROM OIL REFINERIES[29]

Equipment Unit Source	Emission Factors[a]			Emission Rates in Los Angeles Area,[a] tons/day
	$\mu g/m^3$	ppm	lb/1,000 bl	
Catalytic cracking unit				1.9
Fluid	3,600-48,000	3-130	19	1.5
Thermofor	10,800-212,400	9-177	12	0.4
Boilers and process heaters				0.5
Fuel gas			3.1[b]	
Fuel oil			25	
Compressor internal combustion engines			0.11[b]	

[a] Calculated as formaldehyde.
[b] lb/1,000 ft^3 fuel gas.

APPENDIX

TABLE 25

REPORTED ALDEHYDE EMISSIONS FROM VARIOUS SOURCES

Source	Aldehyde Emissions (as Formaldehyde)	Ref.
Amberglass manufacture		
Regenerative furnace, gas fired	8,400 $\mu g/m^3$	60
Brakeshoe debonding (single-chamber oven)	0.10 lb/hr	60
Core ovens		
Direct gas-fired (phenolic resin core binder from oven)	62,400 $\mu g/m^3$	60
Direct gas-fired (linseed oil core binder from afterburner)	<12,000 $\mu g/m^3$	60
Indirect electric (linseed oil core binder from oven)	189,600 $\mu g/m^3$	60
(from afterburner)	<22,800 $\mu g/m^3$	60
Insulated wire reclaiming		
Rubber covered 5/8" o.d.		
Secondary burner off	126,000 $\mu g/m^3$	60
Secondary burner on	6,000 $\mu g/m^3$	60
Cotton-rubber-plastic covered, 3/8" to 5/8" o.d.		
Secondary burner off	10,800-43,200 $\mu g/m^3$	60
Secondary burner on	4,800 $\mu g/m^3$	60
Meat smokehouses		
Pressure mixing burner		
Afterburner inlet	0.04 lb/hr	60
Afterburner outlet	0.22 lb/hr	60
Multijet burner		
Afterburner inlet	0.49 lb/hr	60
Afterburner outlet	0.22 lb/hr	60
Meat smokehouse effluent, gas-fired boiler-firebox as "afterburner"		
Water-tube, 426 hp		
Afterburner inlet	0.22 lb/hr	60
Afterburner outlet	0.09 lb.hr	
Water-tube, 268 hp		
Afterburner, inlet	0.39 lb/hr	60
Afterburner, outlet	0.40 lb/hr	60
Water-tube, 200 hp		
Afterburner, inlet	0.39 lb/hr	60
Afterburner, outlet	0.30 lb/hr	60

(continued)

APPENDIX

TABLE 25 (Continued)

REPORTED ALDEHYDE EMISSIONS FROM VARIOUS SOURCES

Source	Aldehyde Emissions (as Formaldehyde)	Ref.
Locomotive, 113 hp		
Afterburner inlet	0.03 lb/hr	60
Afterburner outlet	0.0 lb/hr	60
HRT, 150 hp		
Afterburner inlet	0.03 lb/hr	60
Afterburner outlet	0.18 lb/hr	60
Meat smokehouse exhaust		
Gas-fired afterburner, inlet	104,400 $\mu g/m^3$	60
Outlet	40,200 $\mu g/m^3$	60
Electrical precipitation system		
Inlet	88,800 $\mu g/m^3$	60
Outlet	56,400 $\mu g/m^3$	60
Mineral wool production		
Blow chambers	109 $\mu g/m^3$	60
Curing ovens		
Catalytic afterburner, inlet	1.90 lb/hr	60
Outlet	0.90 lb/hr	60
Direct-flame afterburner, inlet	2.20 lb/hr	60
Outlet	0.94 lb/hr	60
Wool coolers	32 $\mu g/m^3$	60
Litho oven, inlet	120 $\mu g/m^3$	113
Outlet	32,880 $\mu g/m^3$	113
Outlet	4,680 $\mu g/m^3$	113
Paint bake oven		
Nozzle mixing burner		
Afterburner inlet	0.19 lb/hr	60
Afterburner outlet	0.03 lb/hr	60
Atmospheric burner		
Catalytic afterburner inlet	0.07 lb/hr	60
Catalytic afterburner outlet	0.31 lb/hr	60
Premix burner		
Catalytic afterburner inlet	0.3-0.4 lb/hr	60
Catalytic afterburner outlet	0.2-0.5 lb/hr	60
Phthalic acid plant	135,600 $\mu g/m^3$	113
Phthalicanhydride production unit (multijet burner)		
Afterburner inlet	1.75 lb/hr	60
Afterburner outlet	0.43 lb/hr	60

(continued)

APPENDIX

TABLE 25 (Continued)

REPORTED ALDEHYDE EMISSIONS FROM VARIOUS SOURCES

Source	Aldehyde Emissions (as Formaldehyde)	Ref.
Reclaiming of electrical windings		
(single-chamber incinerator)		
100 hp generator starter	0.08 lb/hr	60
14 pole pieces	0.08 lb/hr	60
Auto armatures	0.13-0.29 lb/hr	60
Auto field coils	0.49 lb/hr	60
(Multiple chamber)		
Auto field coils	0.08 lb/hr	60
Afterburner		
14 generator pole pieces	0.08 lb/hr	60
Varnish cooking kettles		
Four-nozzle mixing burner		
Afterburner inlet	0.30 lb/hr	60
Afterburner outlet	0.11	60
Inspirator burner		
Afterburner inlet	0.29 lb/hr	60
Afterburner outlet	0.02 lb/hr	60
Webb press	480 $\mu g/m^3$	113
	360 $\mu g/m^3$	113
	480 $\mu g/m^3$	113
	1,920 $\mu g/m^3$	113

TABLE 26 INDUSTRIAL OVEN EFFLUENTS[41]

Process	Predominant Solvent Type	Aldehydes (as Formaldehyde) (μg/m³)		Formaldehyde (μg/m³)		Acrolein (μg/m³)		Sampling Point[b]
		Average[a]	Range	Average[a]	Range	Average[a]	Range	
Adhesive coating	Low boiling alkanes	88,800(5)	73,200-106,800			12.5		A
Duplicate tests		3,000(6)	1,200-6,000			12.5		A
Tube coating	Alcohols	5,100(4)	0-12,000	600(2)	0-1,200	12.5		A
Duplicate tests		19,800(6)	1,200-51,600	2,700(4)	1,200-6,000	12.5		A
Auto body painting	Mixed ketones	15,000(4)	4,800-32,400	9,600(4)	4,800-15,600	3,325(2)	3,225-3,425	B
Duplicate tests		27,960(4)	16,800-56,400	8,520(4)	5,280-10,320	1,975(2)	1,825-2,100	B
Container coating	High-boiling alkanes	52,800(6)	33,600-102,000	19,200(3)	14,400-27,600	9,300(2)	8,450-10,125	C
Container coating	High-boiling alkanes	27,000(4)	12,000-34,800	9,600(4)	7,080-11,880	14,000(2)	12,500-15,500	C
		79,200(4)	48,000-134,400	37,200(4)	18,000-62,400	19,500		D
Container coating	Aromatics	22,800(4)	8,400-36,000	3,840(4)	3,000-4,200	1,875(2)	1,775-1,975	
Container coating	High-boiling alkanes and aromatics	33,960(4)	20,400-45,600	15,000(4)	8,400-18,000	7,000(2)	5,250-9,000	C
		60,600(4)	39,600-87,600	26,400(4)	10,800-42,000	11,000(2)	9,750-12,000	E
Container coating	Aromatics	79,200(4)	58,800-120,000	7,800(4)	6,000-10,800	1,575(2)	1,425-1,725	C
		490,800(4)[c]	277,200-820,800[c]	27,600(4)	24,000-32,400	8,225(2)	5,225-11,200	C
Container coating	Aromatics	82,800(4)	45,600-136,800	33,600(4)	16,800-55,200	21,750(2)	18,500-24,750	D
Container coating	Aromatics	60,000(4)	26,400-91,200	25,200(4)	8,400-43,200	11,500(2)	11,000-12,000	D

[a] Number in parentheses represents number of determinations made.

[b] A: From vent near oven entrance; B: From oven; C: Near front of oven at inlet to exhaust system; D: From stack after passing through direct-flame, gas-fired afterburner; E: From stack after passing through catalytic afterburner.

[c] May be in error due to interfering compound.

TABLE 27

CONCENTRATION OF ALDEHYDES IN THE AIR, 1967[126]

Location	μg/m³ Min	μg/m³ Max	μg/m³ Avg	No. of Samples
Alaska				
Fairbanks County	2	12	5	4
Arkansas				
El Dorado	4	20	13	7
Colorado				
Denver	2	21	9	8
Delaware				
Wilmington	7	67	30	11
District of Columbia				
Washington	1	24	8	16
Illinois				
Chicago	1	25	9	18
Indiana				
East Chicago	1	40	17	18
Indianapolis	1	35	13	17
Iowa				
Des Moines	1	16	5	13
Massachusetts				
Boston	2	78	31	12
Michigan				
Detroit	1	129	29	17
Minnesota				
Minneapolis	2	19	8	12
Missouri				
Kansas City	4	18	10	16
St. Louis*	1	92	21	36
New Jersey				
Camden	1	39	12	14
Newark	7	91	22	16
New York				
New York City	1	22	12	12
Ohio				
Cincinnati	1	35	11	22
Cleveland	1	15	6	16
Oklahoma				
Oklahoma City	17	161	79	14
Tulsa	1	151	42	14
Oregon				
Portland	1	5	3	5

(continued)

TABLE 27 (Continued)

CONCENTRATION OF ALDEHYDES IN THE AIR, 1967[126]

Location	µg/m³ Min	Max	Avg	No. of Samples
Pennsylvania				
Philadelphia	1	27	9	11
Pittsburgh	2	36	9	9
Tennessee				
Chattanooga	2	11	6	12
Texas				
El Paso	2	30	9	9
Pasadena	1	81	25	12
Utah				
Salt Lake City	2	19	9	9
Washington				
Seattle	1	16	5	11
West Virginia				
Charleston	1	85	28	16

*Figures given are from two sites.

TABLE 28

CONCENTRATION OF ALDEHYDES IN THE AIR, 1958-67[a]
($\mu g/m^3$)

Location	1958		1959		1960		1961		1962		1963		1964		1966		1967	
	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
Alabama																		
Jefferson County																		.01
California																		
Los Angeles County											1.6							
Los Angeles					.43	.17												
South Pasadena					.32	.13												
Indiana																		
Indianapolis											.13							
Maryland																		
Baltimore													.23	.05	.10	.05		
Massachusetts																		
Boston											.22	.08						
New York																		
Manhattan	.30	.10	.23	.10	.24	.06	.27	.08	.37	.11								
Roosevelt Field													.11	.02				
Pennsylvania																		
Duquesne											.23	.07						
Pittsburgh											.10	.02						

(continued)

TABLE 28 (Continued)

CONCENTRATION OF ALDEHYDES IN THE AIR, 1958-67
($\mu g/m^3$)

Location	1958		1959		1960		1961		1962		1963		1964		1966		1967	
	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
Texas																		
El Paso	←	←	.20	.05[b]														
East El Paso	←	←	.59	.06[b]														
Northwest El Paso	←	←	.52	.06[b]														
Washington																		
Hanford Project, near Richland																	.02	.02

[a] Data compiled from References 5,34,35,58,72,90-92,104,116,149,152,202.

[b] Arrow indicates time period for sample.

TABLE 29

CONCENTRATION OF ALDEHYDES IN THE AIR, 1951-57[a]
($\mu g/m^3$)

Location	1951		1952		1953		1954		1955		1956		1957	
	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
California														
Los Angeles	.40	.14	.32	.20	.90	.18	1.0	.14	.82	.13	1.6	.10		
West Los Angeles									.78	.16				
Los Angeles County													.54	.06
Highland Park									←		.22[b]	.04[b]	→	
Pasadena									1.8	.18				
Rivera									.73	.14	.54	.16	2.2	.06
El Monte													.47	.05
Azusa									.92	.14				
Burbank									.78	.17			.44	.05
									.56	.18			.56	.07
Kentucky														
Louisville													1.3	
Michigan														
Detroit-Windsor	←		1.0[b]											
New York														
Manhattan									.17	.06	.25	.10	.13	.10
Ohio														
Cincinnati	.24	.04												
West Virginia														
Kanawha River Valley	.54	.06												

[a] Data compiled from References 30,116,150,201,202.

[b] Arrow indicates time period for sample.

TABLE 30

CONCENTRATION OF ALDEHYDES[a] IN METROPOLITAN AREAS BY POPULATION, 1958[194]
($\mu g/m^3$)

Metropolitan Area Population	Average Values		Maximum Values	
	Average	Range	Average	Range
Greater than 2,000,000	290	240-340[b]	1,100[b]	1,000-1,200
500,000 to 2,000,000	80		840[b]	140-2,200
Less than 500,000	50[b]		440	160-720

[a] As formaldehyde.
[b] Less than three cities reported in "average."

TABLE 31

COMPARISON OF METHODS FOR THE DETERMINATION OF FORMALDEHYDE[166]

Reagent	max	$\epsilon \times 10^{-3}$	Beer's Law Range (μg)[a]	Dilution Factor[b]	Sensitivity[c]	Color Stability Time	Interferences
o-Aminobenzaldehyde	440	2.5	12-120	2.5	1.0		Aliphatic aldehydes
Schiff	550	3.5		5	0.7	~30 min	
Chromotropic acid	578	15.7	2.0-40	10	1.57	>24 hr	Formaldehyde-yielding compounds
J-acid (dication)	468	21.0	1.5-32	5	4.2	>24 hr	Formaldehyde-yielding compounds
HBT + NBD	610	24		10	2.4		All aldehydes
J-acid (monocation)	612	34	0.88-15	12.5	2.7	10 min	Formaldehyde-yielding compounds
Phenylhydrazine	520	34.2	0.88-15	25	1.4	15 min	

(continued)

TABLE 31 (Continued)

COMPARISON OF METHODS FOR THE DETERMINATION OF FORMALDEHYDES

Reagent	max	$\epsilon \times 10^{-3}$	Beer's law Range(μg)[a]	Dilution Factor[b]	Sensitivity[c]	Color Stability Time	Interferences
HBT	582	48.0	0.62-12.5	10 20	4.8 2.4	20 min	Water-soluble aliphatic aldehydes give molar absorptivities of about 1,800
Phenyl J-acid	660	51.4	0.56-13	12.5	4.1	>24 hr	Formaldehyde-yielding compounds
MBTH	670	65.0	0.5-9.2	10 20	6.5 3.25	>40 min	Water-soluble aliphatic aldehydes, aromatic amines, imino heterocyclic compounds
1-Ethylquinaldinium iodide	608	73[d]	0.40-8.2	10	7.3	30 min	Other aliphatic aldehydes give molar absorptivities of about 1,500 to 15,000
J-acid fluor.	Excit. λ max 470	Emiss. λ max 520	0.01-2			>120 min	Formaldehyde-yielding compounds, acrolein

[a] Beer's law is not obeyed in Schiff and 1-ethylquinaldinium procedures. The Beer's law range is based on 10 ml final volume; lower limits for this range are taken at an absorbance of 0.1.

[b] Dilution factor is the proportion of final volume to test solution volume.

[c] Sensitivity = $\frac{\epsilon \cdot 10^{-3}}{\text{dilution factor}}$.

[d] For 9.9 μ of formaldehyde.